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FLUORINE CONTAINING ELASTOMERS

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PURDUE RESEARCH FOUNDATION

OCTOBER 1952

WRIGHT AIR DEVELOPMENT CENTER

FLUORINE CONTAINING ELASTOMERS

O. R. Pierce
E. T. McBee

Purdue Research Foundation

October 1952

Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

FOREWORD

This is the first annual report issued by the
Purdue Research Foundation describing work under re-
search and development Contract AF 33(038)-20581. It
covers the period from 11 July 1951 to 11 July 1952
and is the first of a series of reports under this
contract to be issued as WADC Technical Reports.

Materials Laboratory, Directorate of Research,
Wright Air Development Center administered this re-
search project under Research and Development Order
No. 617-11, "Synthesis and Evaluation of New Polymers",
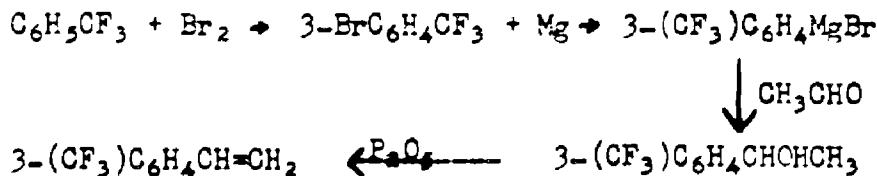with Capt. William Postelnek acting as project engineer.

The personnel assigned to this project were Prof.
O. R. Pierce, Prof. E. T. McBee, Dr. J. C. Siegle,
Dr. M. Levine, Dr. R. Cline, Dr. G. Gorin, Messrs. D.
D. Smith, H. Young, C. G. Hsu, and Mrs. H. Kilbourne.

WADC TR 52-191 Pt 1

ABSTRACT

The nature of the work described in this report embraced the synthesis of two types of materials: (a) fluorine-containing silicones, and (b) fluorine-containing styrenes copolymerized with butadiene. These materials are to be evaluated as low-temperature, fuel-resistant elastomers.

The fluorine-containing silicones were synthesized by routes employing the reaction of a fluorine-containing Grignard reagent with silicon tetrachloride or tetraethyl silicate followed by hydrolysis of the monomer silane obtained. In particular, the monomer, $(C_3F_7CH_2CH_2)_2 SiX_2$ (X=Cl or OEt) was prepared. Also, a perfluoroalkyl Grignard reagent, C_3F_7MgI, was synthesized and its utility in the preparation of perfluoroalkyl silicones studied. At the conclusion of the first year's work, the achievements indicate that the synthesis of highly fluorinated silicone elastomers is feasible and the research is being continued.

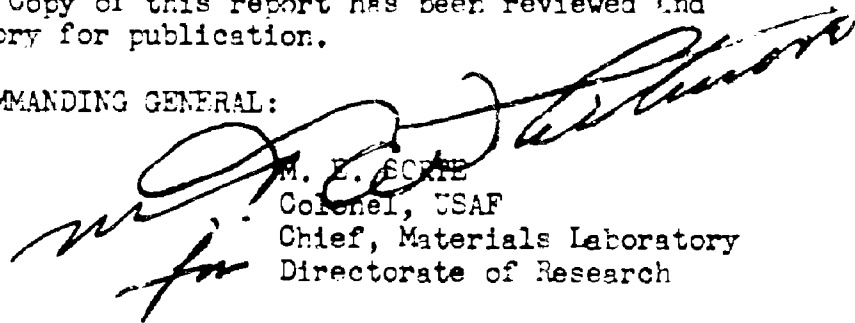The fluorine-containing styrenes were prepared by known methods as follows:

$$C_6H_5CF_3 + Br_2 \rightarrow 3\text{-}BrC_6H_4CF_3 + Mg \rightarrow 3\text{-}(CF_3)C_6H_4MgBr$$

$$\downarrow CH_3CHO$$

$$3\text{-}(CF_3)C_6H_4CH=CH_2 \quad \xleftarrow{P_2O_5} \quad 3\text{-}(CF_3)C_6H_4CHOHCH_3$$

Three monomers were obtained in this way: 3-(trifluoromethyl)styrene, 3,5-bis(trifluoromethyl)styrene, and 2, 5-bis(trifluoromethyl)styrene. These materials were copolymerized with butadiene using an emulsion technique. After preparation of polymer samples was complete, the work was discontinued in this laboratory and no further investigations along this line are contemplated.

PUBLICATION REVIEW

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I. INTRODUCTION

The purpose of the project is to synthesize and evaluate two types of fluorine-containing polymers: (a) styrene-butadiene copolymers, and (b) silicones. These materials are to be evaluated as low-temperature, fuel-resistant purpose materials as suggested by their properties. The first year of the work has been devoted to: (1) the synthesis of monomeric styrenes containing (perfluoroalkyl) substituent groups and preparation of copolymers with butadiene, (2) preparation of organosilanes containing a heptafluoro-pentyl group, and (3) development of synthetic methods for the preparation of organosilanes containing a (perfluoropropyl) group.

Experimental details of the synthesis and polymerization studies conducted during the period June 11, 1951 to June 11, 1952 are presented.

II. General Discussion

A. Synthesis of Monomers

1. Fluorine-containing styrenes.

Three (perfluoroalkyl) substituted styrenes were prepared during this period. These were: 3-(trifluoromethyl)styrene, 3,5-bis(trifluoromethyl)-styrene, and 2,5-bis(trifluoromethyl)styrene. A sample of each monomer (approx. one pound) was submitted to the Materials Laboratory for evaluation. In addition, the synthesis of 2-(trifluoromethyl)styrene was attempted. Experimental details of the laboratory preparations are presented in the following discussion. The fluorine-containing starting materials were obtained from the Hooker Electrochemical Company.

(a) 3-(Trifluoromethyl)styrene.

This material was prepared employing the following reaction sequence:

(1) $C_6H_5CF_3 + Br_2/SbCl_5 \rightarrow 3\text{-}BrC_6H_4CF_3$

(2) $3\text{-}BrC_6H_4CF_3 + Mg/ether \rightarrow 3\text{-}(CF_3)C_6H_4MgBr$

(3) $3\text{-}(CF_3)C_6H_4MgBr + CH_3CHO \rightarrow 3\text{-}(CF_3)C_6H_4CHOHCH_3$

(4) $3\text{-}(CF_3)C_6H_4CHOHCH_3 + P_2O_5 \rightarrow 3\text{-}(CF_3)C_6H_4(CH = CH_2)$

3-Bromo(trifluoromethyl)benzene. The bromination apparatus comprised a glass test tube (4' x 65 mm.) fitted with a water-cooled glass coil immersed in the reaction mixture, gas-dispersion disc, addition funnel and reflux condenser. A solution of antimony pentachloride (274 g., 0.92 mole) and benzotrifluoride (2008 g., 13.7 moles) was placed in the test tube and bromine (644 g., 4.04 moles) was placed in the addition funnel. About 10 g. of bromine was added to the solution, and after the vigorous reaction subsided, the reaction was cooled and chlorine was bubbled in through the disc at a moderate rate. The remainder of the bromine was added over a period of one and one-half hours at the end of which time the solution was dark red. The chlorine

flow was maintained until the solution was nearly colorless. The mixture was poured over 1 kg. of ice, steam-distilled, dried and rectified. The yield of 3-bromo(trifluoromethyl)benzene, b.p. 152°C., was 53%.

Methyl 3-(trifluoromethyl)phenyl carbinol. A mixture of magnesium (25.4 g. 1.02 moles) and anhydrous diethyl ether (200 ml.) was placed in 1-liter, 3-necked flask equipped with a stirrer, reflux condenser, and addition funnel. A solution of 3-bromo(trifluoromethyl)benzene (230 g.; 1.02 moles) and diethyl ether (200 ml.) was added to the flask at a rate such that gentle reflux of the reaction mixture was maintained. When the addition was complete, the reaction mixture was cooled in an ice-water bath and freshly distilled acetaldehyde (53 g., 1.2 moles), dissolved in an equal volume of diethyl ether, was added slowly with stirring. After the addition was complete, the reaction mixture was allowed to warm to room temperature and then poured over 1 kg. of ice to which 30 ml. of concentrated sulfuric acid had been added. The organic layer was separated and the aqueous layer was extracted with two 100 ml. portions of diethyl ether. The organic layer and extracts were combined, washed with water followed by dilute sodium bicarbonate solution and again with water. After drying, rectification of solution produced methyl 3-(trifluoromethyl)-phenyl carbinol, b.p. 100°C. at 15 mm., in 80% yield.

3-(Trifluoromethyl)styrene. A mixture of methyl 3-(trifluoromethyl)-phenyl carbinol (90 g., 0.47 moles), phosphorous pentoxide (5 g.,), and hydro-quinone (2 g.) was placed in a 500 ml. distilling flask. The pressure in the flask was maintained at 130-140 mm. and the reaction temperature was maintained so that distillation of the product occurred. After the reaction was complete, the product was dried by distilling it from phosphorous pentoxide through a short Vigreaux column. The yield of 3-(trifluoromethyl)styrene, b.p. 70°C. at 40 mm., was 67%.

(b) 3,5-bis(Trifluoromethyl)styrene.

This material was prepared similarily to 3-(trifluoromethyl)styrene with the exception that the bromination was conducted at 120-130°C. in a flask. The conversion to 5-bromo-3,5-bis(trifluoromethyl)styrene was 50%. Other reaction yields were similar.
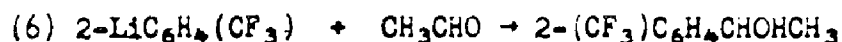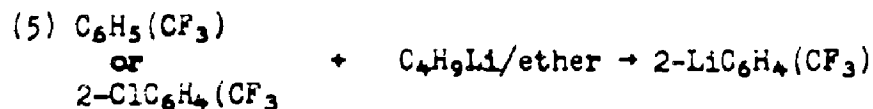
(c) 2,5-bis(Trifluoromethyl)styrene.

This material was prepared in a manner similar to that described for 3,5-bis(trifluoromethyl)styrene. The conversion to the 2-bromo-1,4-bis(trifluoromethyl)benzene was 35%. All other reaction yields were similar.

Physical constants of the styrenes and different preparative techniques are described elsewhere (1,2).

(d) Attempted Synthesis of 2-(Trifluoromethyl)styrene.

The starting materials, benzotrifluoride and 2-chlorobenzotrifluoride, were obtained from the Hooker Electrochemical Company. The syntheses investigated are illustrated as follows:

(5) $C_6H_5(CF_3)$
    or $\qquad$ + C_4H_9Li/ether → $2-LiC_6H_4(CF_3)$
    $2-ClC_6H_4(CF_3$

(6) $2-LiC_6H_4(CF_3)$ + CH_3CHO → $2-(CF_3)C_6H_4CHOHCH_3$

(7) $2-(CF_3)C_6H_4CHOHCH_3$ + P_2O_5 → $2-(CF_3)C_6H_4CH = CH_2$

Procedure (1). The experiment was conducted using 1 mole of butyl lithium as prepared in Organic Reactions (3). One mole of benzotrifluoride was added at room temperature and after a small amount of butane evolution the mixture was refluxed for 12 hours. The solution was cooled to 0°C. and one mole of freshly distilled acetaldehyde was slowly added. The solution was allowed to come to room temperature, then refluxed for two hours. The complex was hydrolyzed in cold water to which a small amount of hydrochloric acid had been added. The ether layer was separated and the water layer was extracted three times with

ether. The ether washings were added to the initial ether solution and the combined solution was fractionated using a Todd precise fractionation assembly (12 mm. barrel, packed with 1/8 in. glass helices). The following fractions were collected after the ether was removed:

Cut	B.P. (°C.)	Vol. (ml.)
1	36 - 100.5	32.5
2	100.5-101.5	20
3	91/15 mm.	1
4	91-94°/15 mm.	28

Cut 1 = forerun of ether and benzotrifluoride
Cut 2 = benzotrifluoride
Cut 3 = forerun
Cut 4 = product

The product was shown to be a mixture of alcohols by cryoscopic measurements. These materials were probably the isomeric (trifluoromethyl)-phenyl methyl carbinols.

The mixed alcohols were dehydrated with phosphorous pentoxide and it was found that the mixed styrenes obtained in this manner could not be separated by rectification. It is concluded that metalation of benzotrifluoride with butyl lithium produces a mixture of metalated materials which cannot be employed for the synthesis of 2-(trifluoromethyl)styrene in satisfactory yield.

Procedure 2. n-Butyl lithium was prepared exactly as described in Organic Reactions (3) using 8.6 g. (1.25 gram atoms) of lithium and 68.5 g. (0.5 moles) of n-butyl bromide. The n-butyl lithium was filtered under nitrogen into a 1 l., 3-necked flask equipped with a stirrer, addition funnel and condenser, and 2-chloro-(trifluoromethyl)benzene (45 g., 0.25 moles) was added all at once. Vigorous boiling occurred with the evolution of a gas being noted through a bubbler attached to the exit of the condenser. This gas was probably butane. When the initial reaction had subsided, the mixture was allowed to stir at room temperature for 8 hours., and it was then poured into

a slurry of dry ice and ether for use as a carbonation agent. About 500 ml. of water was added and the resulting two layers were separated. The water layer was extracted three times with 100 ml. portions of ether. The original ether layer and the washings were discarded. The ether washings were combined, and the ether removed by distillation. The residue partially solidified upon cooling. After three recrystallizations from ligroin (110°) the product melted sharply at 109-109°C. This is the same as the melting point reported by Roberts and Curtin (4) for 2-(trifluoromethyl)benzoic acid and establishes that the reaction mixture was in part, the desired 2-(trifluoromethyl)phenyl lithium. However, conversion of this material to the corresponding methyl carbinol produced a mixture which could not be separated. Consequently no further work was initiated along this line of investigation.

2. Hexafluorobutadiene.

A small quantity of this material was prepared for use in copolymerization studies with the fluorine-containing styrenes. However, a later evaluation of the research program precluded this monomer from further study. Experimental details of the synthesis are given in the following discussion. The reactions sequence employed is illustrated as follows:

$$(8) \quad CCl_2 = CClCCl = CCl_2 + PbF_4 \rightarrow C_4Cl \; x \; Fy$$
$$(x + y = 10)$$

$$(9) \quad C_4Cl \; x \; Fy + Zn/EtOH \rightarrow C_4F_6$$
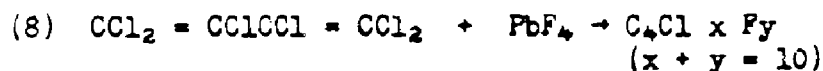
The hexachlorobutadiene used was obtained from the Hooker Electrochemical Company.

(a) Fluorination of Hexachlorobutadiene.

Hexachlorobutadiene (5 kg.) in a stream of nitrogen was passed over lead tetrafluoride contained in eight nickel trays connected in series by means of copper tubing. Each tray contained 20 moles of the salt and vaporization of hexachlorobutadiene was effected in the first tray. The temperature

of the reaction chambers was 200° ± 25°C., and the pressure was maintained as closely as possible at 150 mm., by means of a water aspirator. During the addition, the formation of chlorine gas made it impossible to hold the pressure at anything less than 150 mm. The time required for the addition of all the starting material was six hours, and the nitrogen flow was maintained for an additional 1 1/2 hours.

The product was collected in two nickel traps, one cooled by ice water, the other by a dry ice-trichloroethylene slush. The contents of the traps were combined and transferred to a separatory funnel where they were washed twice with 1 l. portions of 20% aq. potassium hydroxide and twice with 1 l. portions of water. The washed material was dried over calcium chloride.

Rectification of the dried material was effected through a 6 ft. Stedman column having an efficiency of 100 theoretical plates to give the following:

Cut No.	B.P., (°C.)	Vol., ml.	Compound
1	27-60	70	Forerun
2	60-64	550	$C_4Cl_2F_8$
3	64-96.5	135	Intermediate
4	96.5-98	800	$C_4Cl_3F_7$
5	98-131	65	Intermediate
6	131-133	550	$C_4Cl_4F_6$
Res.	133 over 200	---	$C_4Cl_5F_4$ + C_4Cl_6

(f) Dehalogenation Reactions.

(1) A 2-l., 3-neck flask was equipped with a mercury-sealed stirrer dropping funnel and a Friedrich condenser. The outlet of the condenser was connected to a trap which was cooled by means of a dry ice-trichloroethylene slush. Ethanol (700 ml.) was placed in the flask and heated to reflux. Zinc dust (195 g., 3.0 moles) was added with rapid stirring and then tetrachloro-hexafluorobutane (450 g., 1.5 moles) containing a trace of dissolved iodine was added slowly. The resulting solution was allowed to reflux with rapid

stirring for 18 hours after which time 72 g. of material had collected in the cooled trap. Rectification of this material yielded 50 g. (20%) of hexafluoro-butadiene, b.p. 6-7°.

(2) A mixture of butanol (200 ml.) and ethanol (300 ml.) was placed in a 1 l. flask and brought to reflux. Zinc dust (65.0 g., 1.0 mole), previously activated by washing with dilute hydrochloric acid, water and ethanol, was added with rapid stirring, and then tetrachlorohexafluorobutane (100 g., 0.33 mole) was added slowly. The resulting solution was allowed to reflux with stirring for 36 hours. Twenty grams of material had collected in the trap. Since there was so little product it was not rectified, but was saved and combined with the product obtained in Part (3).

(3) Ethanol (1 l.) was heated to reflux. Zinc dust (195 g., 3.0 moles) was added with rapid stirring, and then tetrachlorohexafluorobutane (320 g., 1.06 moles) was added dropwise over a 45 minute period. The resulting solution was allowed to reflux with stirring an additional 18 hours, at the end of which time 50 g. of material had collected in the cold trap. This was combined with the material from Part (2) and rectified. Rectification yielded 50 g. of hexafluorobutadiene, b.p. 6-7°.

The over-all yield (parts 1, 2, and 3) from 870 g. (2.88 moles) of tetrachlorohexafluorobutane was 100 g. (21%) of hexafluorobutadiene.

(4) Acetone (400 ml.) and potassium iodide (140 g., 0.84 mole) were placed in a 1 l. flask and the acetone brought to reflux. Tetrachlorohexa-fluorobutane (50 g., 0.16 mole) was added dropwise to the refluxing acetone solution. After all the starting material was added the solution was allowed to reflux for 20 hours, at which time it had become dark reddish-brown in color. However, there was no material in the cooled trap.

Water (250 ml.) was added, and the solution refluxed several hours

more. The red color lightened, but there was still no low-boiling material formed.
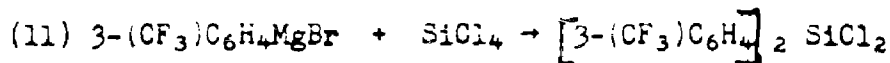
The flask was changed to one of 2 l. capacity, another liter of water was added and the solution was further refluxed for several hours. The solution became colorless, and a second, heavy layer was noticed when stirring was discontinued, but there was no material in the cooled trap. No further investigations using acetone were made.

3. Fluorine-containing Silanes.

The synthesis of three types of silanes was investigated during the past year. These materials were: (1) (perfluoroalkyl)phenyl silanes, (2) (3,3,4,4,5,5,5-heptafluoropentyl) silanes, and (3) (heptafluoropropyl) silanes. In addition, investigations were begun in the preparation of fluorine-containing propyl and isopentyl substituted silanes but later discontinued in favor of the former materials. Experimental details are given in the following discussion.

(a) (Perfluoroalkyl)phenyl silanes.

These materials were prepared as illustrated by the following reaction sequence:

(10) $3\text{-}BrC_6H_4CF_3$ + Mg/Ether → $3\text{-}(CF_3)C_6H_4MgBr$

(11) $3\text{-}(CF_3)C_6H_4MgBr$ + $SiCl_4$ → $\left[3\text{-}(CF_3)C_6H_4\right]_2 SiCl_2$

The starting material, benzotrifluoride, was obtained from the Hooker Electrochemical Company and brominated as described under Section 1 of the report.

$\left[(Trifluoromethyl)phenyl\right]$ chlorosilanes. A crystal of iodine and 12.2 gms. (0.5 gram-atom) of magnesium turnings were placed in a 500 ml. 3-necked round-bottom flask equipped with a dropping funnel, mercury-sealed stirrer, and a water-cooled condenser. The system was thoroughly flamed out while being purged with dry nitrogen and, after cooling, was closed to the atmosphere. Enough anhydrous ether was introduced through the dropping funnel

to cover the magnesium. Then 113.0 gms. (0.5 mole) of 3-bromo(trifluoromethyl)-benzene, dissolved in 100 ml. of anhydrous ether, was added dropwise. The Grignard solution formed was then cooled in a water-ice bath and a solution of 42.5 gms. (0.25 mole) of silicon tetrachloride in ether added dropwise. The cold bath was removed as soon as the heat of reaction had been dissipated. The magnesium salts were filtered off through a sintered glass funnel and the filtrate rectified in a 12 mm., glass-helix-packed Todd column. The ether was removed by distillation at atmospheric pressure and the residue distilled at 2-3 mm. pressure. There was obtained 6.3 gms. (0.0225 mole) of [3-(trifluoromethyl)phenyl] trichlorosilane, b.p. 55-56°C. (2-3 mm.), n_D^{20} 1.4677, d_4^{28} 1.423 (9.0% yield), 46.4 gms. (0.119 mole) of bis [3-(trifluoromethyl)phenyl] dichlorosilane, b.p. 114-116°C/(2-3 mm.) with a yield of 47.7%, and 14.5 gms. (0.0291 mole) of tris[3-(trifluoromethyl)phenyl] chlorosilane, b.p. 161-164°C. (2-3 mm.) with an 11.6% yield, giving a total yield of 68.3%.

[(Trifluoromethyl)phenyl] polysiloxanes. All hydrolyses were conducted in the following manner: a solution of 0.10 mole of the chlorosilane in 25 ml. of toluene was added dropwise to a rapidly stirred heterogeneous mixture of 100 ml. of water, 75 ml. of t-amyl alcohol, and 25 ml. of toluene. After the addition was completed, the mixture was stirred for an additional thirty minutes. The organic layer was separated and washed with one 100 ml. and two 50 ml. portions of water. The water washes and the original aqueous layer were combined and washed with three 25 ml. portions of toluene. The toluene washes and the original organic layer were combined and dried with Drierite. The material was then distilled at atmospheric pressure to remove the toluene and t-amyl alcohol.

Hydrolysis of [3-(trifluoromethyl)phenyl] trichlorosilane. After removal of the toluene and the t-amyl alcohol, there remained from 28.0 gms. (0.10

mole) of [3-(trifluoromethyl)phenyl]trichlorosilane, 17.5 gms. of a cloudy, translucent, sticky material with a very high viscosity. On the basis of the empirical formula $(CF_3C_6H_4SiO_{1.5})_x$, which can be assigned to the crosslinked polymer from the hydrolysis of the trichlorosilane and spontaneous condensation of the hypothetical triol, this represented a yield of 89%.

Anal. for $(C_7H_4F_3O_{1.5}Si)_x$, Calcd.: C, 42.64/; H, 2.04%

Found: C, 42.65/; H, 2.15%.

A portion of this material was subjected to a temperature of 116°C. for six days. It gradually became hard and brittle and assumed a glass-like form. However, even at this stage, it was soluble in ether. Analysis of this material gave: C, 42.60% and H, 1.93%.

Hydrolysis of bis[3-(trifluoromethyl)phenyl]dichlorosilane. Thirty-eight and nine-tenths grams (0.10 mole) of bis[3-(trifluoromethyl)phenyl]-dichlorosilane was hydrolyzed under the given conditions. The residue left after the toluene and t-amyl alcohol were removed by distillation at atmospheric pressure was distilled at 3 mm. pressure. The distillation started at 110°C. and the temperature rose steadily throughout the distillation until it reached 290°C., at which point the distillation was stopped. Four fractions were obtained:

Fraction No.	n_D^{20}	Weight, gms.	Analysis, % C	H
1	1.5127	1.9	64.70	3.17
2	1.5044	0.5	61.46	3.49
3	1.4919	8.8	52.17	2.86
4	1.4940	11.9	50.46	2.29

Possible products of this reaction by analogy with the products of the hydrolysis of diphenyldichlorosilane and condensation of the resulting diol are:

Compound	Formula	Composition, %	
		C	H
Bis[3-(trifluoromethyl)-phenyl]silicanediol	$(CF_3C_6H_4)_2Si(OH)_2$	56.94	3.41
Hexakis[3-(trifluoromethyl)-phenyl]cyclotrisiloxane	$(CF_3C_6H_4)_6Si_3O_3$	50.30	2.41
Octakis[3-(trifluoromethyl)-phenyl]cyclotetrasiloxane	$(CF_3C_6H_4)_8Si_4O_4$	50.30	2.41

Hydrolysis of tris[3-(trifluoromethyl)phenyl]chlorosilane. Forty-nine and eight-tenths grams (0.10 mole) of tris[3-(trifluoromethyl)phenyl]chloro-silane were hydrolyzed in the prescribed manner. After the toluene and t-amyl alcohol were removed, the residue was distilled at 3 mm. and four fractions collected. The first two fractions were unreacted chlorosilane; and the fourth was a slightly yellow, viscous material that distilled at 240-245°C. (3 mm.). It froze to a clear yellow glass in the condenser and the water had to be removed and the condenser heated with a flame before the material would flow in-to the receiver. After eighteen hours at room temperature, this material soli-dified completely with evidence of crystal formation. When recrystallized from acetic acid, the compound had a melting point of 78-79°C. (uncorrected). Analysis gave: C, 52.78%; H, 2.66%. Tris[3-(trifluoromethyl)phenyl]silanol has the composition: C, 52.51%; H, 2.66%.

Two attempts were made to condense tris[3-(trifluoromethyl)phenyl]si-lanol to hexakis[3-(trifluoromethyl)phenyl] disiloxane. In one of these, the silanol was dissolved in benzene; concentrated hydrochloric acid was added; and the mixture was refluxed for three hours. In the other attempt, the silanol was dissolved in acetic acid; the solution was heated to boiling; and concentrated nitric acid was added dropwise until the solution became turbid. In both cases, the material recovered had a melting point of 84-85°C. (uncorrected). In the latter case, the material was analyzed and gave the following results: C, 53.50%;

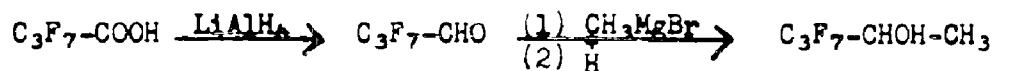H, 2.65%. Hexakis[3-(trifluoromethyl)phenyl]disiloxane has the composition:
C, 53.51%; H, 2.57%.

(b) Preparation of (3,3,4,4,5,5,5-Heptafluoropentyl) Halo and Ethoxysilanes

The general reaction sequence is as follows:

(12)

$$C_3F_7-COOH \xrightarrow{LiAlH_4} C_3F_7-CHO \xrightarrow[(2)\ H]{(1)\ CH_3MgBr} C_3F_7-CHOH-CH_3$$

$$\downarrow P_2O_5$$

$$C_3F_7-CH_2MgBr \xleftarrow{Mg} C_3F_7-CH_2-CH_2Br \xleftarrow[Activated\ carbon]{HBr} C_3F_7-CH = CH_2$$

$$\downarrow SiCl_4 \ or \ Si(OEt)_4$$

$$(C_3F_7-CH_2-CH_2)_xSiCl_y \quad (x + y = 4) \qquad (C_3F_7-CH_2-CH_2)_xSi(OC_2H_5)_y \ (x + y = 4)$$
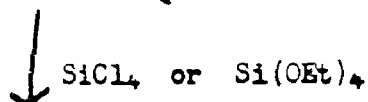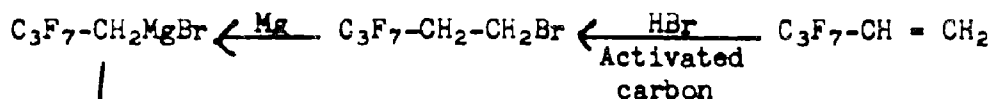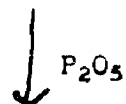
The starting material heptafluorobutyric acid was obtained from the Minnesota
Mining and Manufacturing Company.

Heptafluorobutyraldehyde. Sixty grams (1.58 mole) of lithium alumi-
num hydride (powdered) were added to 3.5 lbs. of dry ether in a 5 liter, 3-
necked flask equipped with dropping funnel, reflux condenser and mercury-
sealed stirrer. After cooling the solution in an ice-bath a mixture of 440 g.
(2.06 mol.) of heptafluorobutyric acid in 0.5 lb. of ether was added at such a
rate that the ether did not reflux. Stirring was continued for an additional
30 minutes and hydrolysis of the lithium aluminum hydride brought about by
very slow addition of 30-40 ml. of water. The reaction mixture was poured
into a mixture of 2 kg. of ice and 350 ml. of concentrated sulfuric acid with
stirring. Additional water was added until all inorganic salt went into solu-
tion. The organic layer was combined with several ether extracts of the aqueous
layer and the mixture subjected to distillation to remove ether. The residue was
diluted with one liter of concentrated sulfuric acid at ice-bath temperature.

Distillation through a short column packed with 1/4 inch glass helices into a receiver cooled with ice water and equipped with a drying tube gave 245 g. (1.24 mole) of heptafluorobutyraldehyde boiling at 28-31°C. (60% yield).

3,3,4,4,5,5,5-Heptafluoro-2-pentanol. In a 2-liter 3-neck flask equipped with mercury-sealed stirrer, glass inlet tube and dry ice condenser was placed 23.4 g. of magnesium turnings and 1 lb. of dry ether. In a dry nitrogen atmosphere, methyl bromide was admitted until all of the magnesium was dissolved. The flask was cooled in an ice-bath and 100 g. (0.505 mole) of heptafluorobutyraldehyde dissolved in an equal volume of dry ether was added slowly. The solution was allowed to stir overnight and then it was refluxed for an hour. After cooling the solution in an ice-bath, 72 ml. of concentrated sulfuric acid and 480 ml. of water were added slowly to hydrolyze the complex. The ether layer was combined with several ether extractions of the aqueous layer and dried over anhydrous sodium sulfate. Removal of the ether by distillation followed by distillation of the residue through a Todd fractionation column (12 mm. barrel packed with 1/8 in. glass helices) gave 73.6 g. (68.5%) of 3,3,4,4,5,5,5-heptafluoro-2-pentanol boiling at 100-101°C., n_D^{23} = 1.309.

3,3,4,4,5,5,5-Heptafluoro-1-pentene. In a 200 ml. round-bottom flask attached to a reflux condenser surmounted with a drying tube was placed 50 g. (0.23 mole) of 3,3,4,4,5,5,5-heptafluoro-2-pentanol. The flask was cooled in an ice-bath and 54.1 g. (0.38 mole) of phosphorus pentoxide added portionwise (about 12 g. at a time) with shaking in order to effect a homogeneous solution. The mixture was then allowed to warm up and stand overnight. The flask was heated by means of a Woods metal bath at 130-140° for 45 minutes and since no refluxing occurred it was concluded that all the alcohol had combined with the phosphorus pentoxide, so that heating the mixture at a higher temperature would give decomposition to the olefin and no evolution of alcohol.

The condenser was then set downward leading into a receiver being immersed in a dry ice bath. The flask was heated at 245-250° for 2.5 hours, 260-275° for 2.5 hours, and finally at 300° for 0.5 hour, the temperature being measured in the Woods metal bath. The olefin distillate weighed 39.6 g. (0.20 mole, 87%) and when redistilled through a short Vigreaux column gave 37.5 g. (0.19 mole, 83%) boiling at 30.0° at 735.4 mm.

The results of experiments conducted on larger scales are summarized in Table I. Consistently high yields of olefin were obtained. The procedure employed was to cool the alcohol in an ice-bath, add approximately the same weight of phosphorus pentoxide portionwise (4-5 portions), let the mixture stand and warm up overnight, and decompose the alcohol-P_2O_5 complex by heating the 500 ml. flask with a heating mantle, the flask being attached to a 7 inch Vigreaux column leading into a condenser attached to receiver immersed in a dry ice cooled bath. It did not appear that appreciable high-boiling impurity could enter the receiver by this technique.

Table I

Exp.No.	Wt. alcohol	Wt. P_2O_5	Heating periods Time,hrs.	Temp.°C[*]	Wt. olefin
1	200 g. (0.93 mole)	175.5 g.	2 2.6 2.5 3.5	32-189 185-197 197-245 245-341	173.5 g. (0.88 mole) 95%
2	208.4 g. (0.97 mole)	182.1 g.	7 21 8 20	106-197 171.198 250-270 300-343	182.8 g. (0.93 mole) 96%
3[X]	216.9 g. (1.01 mole)	213.4 g.	7 16	190-250 250-340	178.3 g. (0.91 mole) 90%

[*]Temperature measured by means of a thermometer well in the
round-bottom reaction flask.
[X]A 1-liter flask was used in this experiment in place of the
usual 500 ml. flask.

The 3,3,4,4,5,5,5-heptafluoro-1-pentene is a nearly odorless liquid boiling at 31.0° at 742.8 mm. as fractionated through a Todd column. The refractive index is below 1.30. An acetone solution of the olefin is oxidized when added to 2% aqueous permanganate. An infra-red spectrum of the olefin indicated the presence of a double bond. Samples sent in for analysis were specially purified by shaking with aqueous bicarbonate followed by drying over drierite and distillation from P_2O_5 through a Todd Column packed with glass helices.

Analysis: Calculated for $C_5H_3F_7$: C, 30.62; H, 1.54. Found: C, 29.89; H, 1.96. Analysis of second sample. Found: C, 30.61, 30.75; H, 1.72, 1.65.

Additional attempts to prepare the olefin by different techniques are summarized:

(1) In a three-necked flask equipped with a dropping funnel and reflux condenser,whose outlet led to a dry-ice cooled trap,was placed 30 ml. of concentrated sulfuric acid. Twenty grams (0.094 mole) of 3,3,4,4,5,5,5-heptafluoro-2-pentanol were added slowly and the temperature gradually raised to 180°, but there was no evidence of olefin formation. An additional 2.2 g. (0.010 mole) of alcohol and 30 g. of phosphorus pentoxide were added and the temperature raised to 220-250°. The distillate was found to have only 0.6 ml. of the desired pentene.

(2) A mixture of 9 g. (0.064 mole) of phosphorus pentoxide, 20 g. (0.093 mole) of 3,3,4,4,5,5,5-heptafluoro-2-pentanol, and 10 ml. of di-n-butyl ether was refluxed for several hours in a 100 ml. round-bottom flask. Distillation of the reaction mixture followed by rectification of the distillate gave only starting material.

(3) A mixture of 35 g. (0.25 mole) of phosphorus pentoxide and 60 ml. of di-n-butyl ether was placed in a 500 ml. three-necked round bottom flask

equipped with mercury seal stirrer, ground glass plug, and condenser with gas delivery tube to a dry-ice trap. One hundred grams (0.47 mole) of 3,3,4,4,5,5,5-heptafluoro-2-pentanol were added with stirring and the mixture refluxed for eight hours. The dry-ice trap collected 29 g. of colorless liquid which on fractionation yielded a small amount of liquid boiling at about 0°C. This liquid contained an olefin which reacted with bromine readily but the material was not identified. Distillation of the reaction mixture yielded only original alcohol.

(4) A mixture of 10 g. (0.047 mole) of 3,3,4,4,5,5,5-heptafluoro-2-pentanol and 3 g. (0.021 mole) of phosphorus pentoxide was warmed to 80-100° for one hour. When the temperature was raised to 130-137°, 4.4 g. of the original alcohol was obtained by distillation. Above 225° the mixture yielded 2.2 g. of the desired pentene in the distillate.

(5) In a three-necked flask equipped with Claisen head and condenser, thermometer well and dropping funnel were placed 35 ml. of phosphoric acid and the mixture heated to 250°. The dropwise addition of 20 g. of 3,3,4,4,5,5,5-heptafluoro-2-pentanol caused a colorless liquid to distill over. Fractionation of this distillate gave 16 g. of original alcohol boiling at 98-101°.

3,3,4,4,5,5,5-Heptafluoro-1-bromopentane. Hydrogen bromide gas has been found to add to 3,3,4,4,5,5,5-heptafluoro-1-pentene at 120-140° in the presence of activated carbon to give good yields of 3,3,4,4,5,5,5-heptafluoro-1-bromopentane. The vapor phase technique evolved is a simple version of the method used by Park et al (5) to add hydrogen halides to completely fluorinated olefins.

The apparatus is designed to allow the olefin to recycle through the catalyst, maintained at any temperature from room temperature to 350° and subjected also to a stream of HBr, until all of the olefin has been converted to bromide. Gases from the reaction tube pass into water cooled condenser and

D

EXIT HBr

24/40

VARIAC

C

24/40

HBr INLET
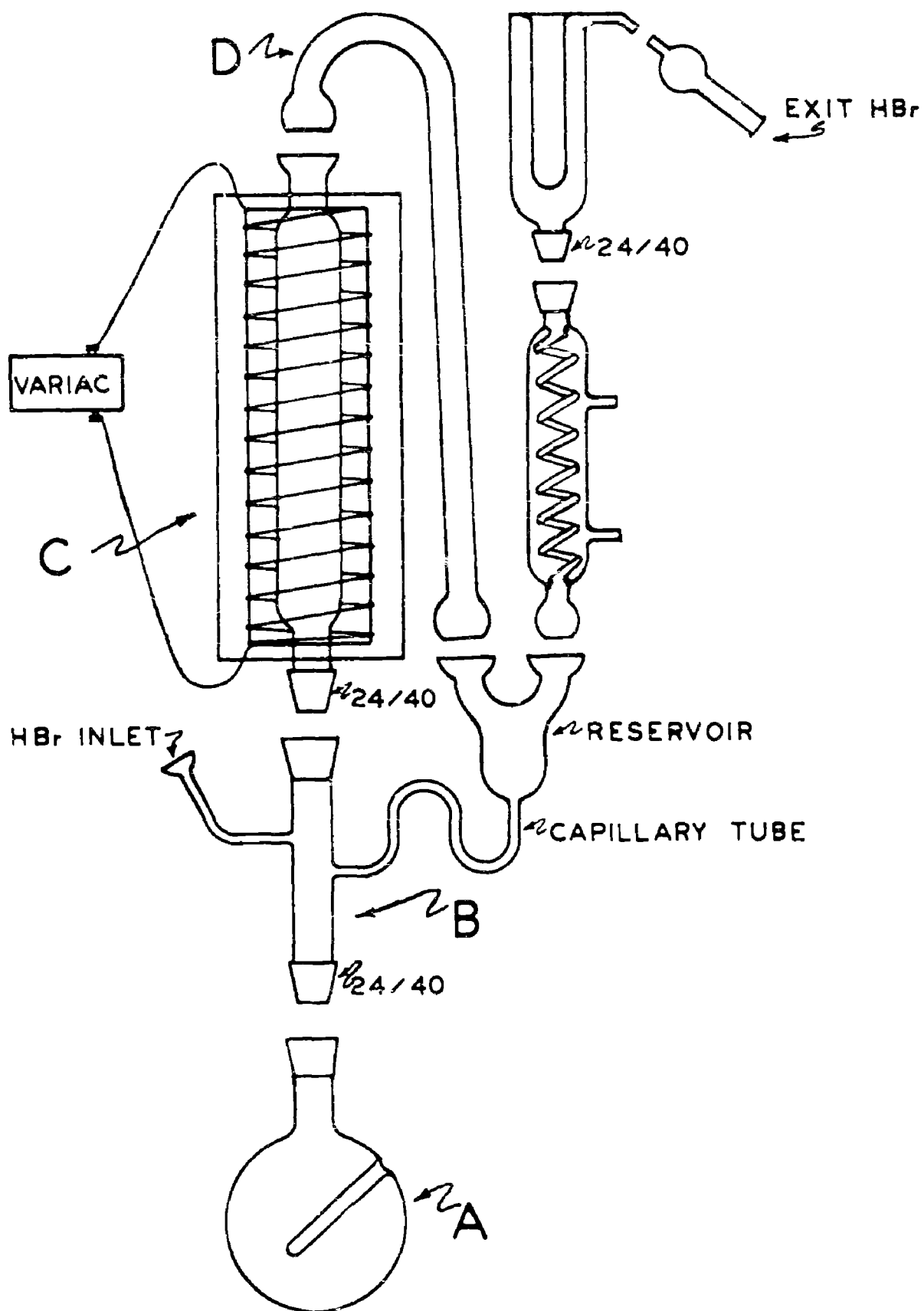
RESERVOIR

CAPILLARY TUBE

B

24/40

A

FIGURE 1
APPARATUS FOR ADDITION OF HYDROGEN BROMIDE

then into a dry ice cooled condenser vented to the atmosphere. Thus the olefin cannot escape from the apparatus although most of the HBr can escape. The olefin makes a complete cycle in all-glass apparatus made easy to construct by the use of ball joints. A capillary U tube is incorporated in the gas pathway which functions as a valve permitting liquid to go one way but blocking the passage of gases the opposite way.

Hydrogen bromide gas is obtained from a cylinder and purified by passage first through a tube packed with calcium chloride and phosphorus pentoxide, then through a wash bottle containing tetralin to take out bromine, and finally through a tube packed with glass wool and silica gel. The rate of flow is estimated from the rate of bubbling through the tetralin.

The rate of flow of olefin into the reaction chamber is regulated by adjusting the voltage applied to a heating mantle placed under the round bottom flask containing the olefin.

The catalyst consists of 20-30 or 20-48 mesh Columbia activated carbon freshly reactivated before each run by heating at approximately 200° for 3 hours under vacuum, employing a round bottom flask equipped with thermometer well; and after the heating period the catalyst mass is allowed to cool under vacuum before stoppering and setting aside. The catalyst at the end of a run is discarded. In some runs 20-30 mesh calcium sulfate was added to the carbon prior to activation to serve as a promoter.

The essential parts of the vapor phase apparatus are as follows:

1. Olefin Vaporizing Flask, A.- A round bottom flask equipped with thermometer well, heated by means of a glass-col mantle, and attached to the tube assembly B by means of a standard taper joint.

2. Tube Assembly, B.- This assembly permits the HBr to mix with olefin from the olefin vaporizing flask and the mixture of gases to pass

into the bottom of the reaction tube. Below the HBr inlet tube is attached the capillary U tube which is in turn joined to a reservoir. The reservoir has a socket joint and a connecting tube provided with a socket joint.

3. Reaction Tube, C.- This tube has a 24/40 joint at the bottom and a socket joint at the top. It is 400 mm. long and 32 mm. in diameter and thus designed to hold about 140 g. of activated carbon (20-48 mesh). It is constricted at the bottom so as to contain the catalyst. The tube is heated by means of a furnace consisting of two concentric tubes, the innermost one wrapped with Chromel heating wire and the outer one serving as an insulator. A thermometer is suspended between the inner and outermost tubes. The tubes are positioned in a vertical position by means of two asbestos plates fastened to each end of the concentric tube assembly. If desired, heat loses can be minimized by wrapping the outer glass tube of the furnace with glass wool.

4. Connecting Tube, D.- When the tube assembly B and reaction tube C are joined this tube is bent to make the proper connection between these two elements. This connecting tube has ball joints at each end to fit into the socket joints on the reaction tube C and tube assembly B.

5. Condenser System.- An allihn water condenser is fitted directly above the reservoir in the tube assembly B by means of a ball and socket joint. The water condenser is then joined at the top with a bent connecting tube, in turn connected with a dry ice condenser. The outlet from the dry ice condenser, is connected to rubber tubing which carries the escaping HBr to a laboratory hood. The procedure used in conducting an experiment was as

follows: The apparatus was completely assembled making sure all joints were properly lubricated. The connecting tube was then removed and catalyst quickly poured into the reaction tube. The connecting tube was quickly put back in place and the furnace for the reaction tube turned on. Dry ice was placed in the dry ice cooled trap and olefin was placed in the olefin vaporizing flask. The HBr was then allowed to pass into the apparatus and when this gas began to condense at the dry ice cooled trap the mantle for the olefin containing flask was turned on (voltage set at 26). This procedure allows the catalyst to become saturated with HBr at nearly the desired reaction temperature before the olefin is allowed to enter the catalyst. The progress of the addition reaction is easily followed by observing the increasing temperature of the refluxing olefin-product mixture in the round-bottom flask. At the end of the run this liquid boils at 97°, the boiling point of pure heptafluoropentyl bromide. It was found expedient to stop heating the olefin vaporizing flask when the temperature of this refluxing mixture reaches 96° since the additional time required to raise the boiling point an additional degree might bring about excessive decomposition of the bromide on the catalyst. When heating of the olefin vaporizing flask is stopped, the reaction chamber is heated to about 300° to drive out any adsorbed bromide. The crude product is purified by shaking with aqueous bicarbonate, drying over drierite, and distillation from phosphorus pentoxide through a glass helice packed Todd column. The pure product is thus suitable for use in the Grignard Reaction.

Table II summarizes the results of experiments in HBr addition to heptafluoropentyl bromide using the large apparatus just described.

Table II

Exp. No.	Wt. Olefin	Catalyst	Reaction tube temp.	[a]Contact time	Yield pure bromide
12	150 g.	20-30 mesh 124 g. carbon 37 g. CaSO₄	107-125°	4 hr.	91.1 g., 43%
13	181.6 g.	"	107-131°	7 hr.	178.9 g., 70%
14	197.7 g.	"	120-125°	6 hr.	213.1 g., 77%
15	223.4 g.	"	126-148°	7 hr.	223.4 g., 72%
16	217.3 g.	"	126-131°	9 hr.	236.4 g., 77%
17	198.1 g.	"	113-138°	10 hr.	209.9 g., 76%
18	285.0 g.	"	118-137°	14.5 hr.	310.0 g., 77%
19	243.7 g.[b]	"	127-132°	9.5 hr.	261.8 g., 76%
21	304.3 g.[b]	20-48 mesh 137 g. carbon	134-142°	11.2 hr.	325.8 g., 76%

[a] Time of contact of both olefin and HBr with catalyst.
[b] Olefin specially purified by shaking with aqueous bicarbonate, drying with drierite, and distilling from P_2O_5 through a Todd column.

Pure 3,3,4,4,5,5,5-heptafluoro-1-bromopentane is a colorless liquid having a characteristic odor and boiling at 97-98°. The refractive index is below 1.30. This bromide gives a trace of silver bromide precipitate when boiled five minutes with alcoholic silver nitrate.

Analysis. Calculated for $C_5H_4F_7Br$: C, 21.67; H, 1.46; Br, 28.85. Found: C, 21.50; H, 2.02; Br, 28.72.

Attempt to Add Hydrogen Iodide to 3,3,4,4,5,5,5-Heptafluoro-1-pentene. A mixture of 2 ml. of hydrogen iodide (0.069 mole) and 10.0 g. (0.051 mole) of heptafluoropentene was sealed in a Carius tube and allowed to stand 48 hours. Distillation of the reaction mixture gave only starting material.

3,3,4,4,5,5,5-Heptafluoropentyl Grignard Reagent. Into a 100 ml.

three-necked flask equipped with mercury seal stirrer, condenser, drying tube, nitrogen inlet, and pressure regulator was placed 0.535 g. (0.022 mole) of magnesium ribbon. After drying the flask and contents by heating in a nitrogen atmosphere, 50 ml. of anhydrous ether and 6.09 g. (0.022 mole) of 3,3,4,4,5,5,5-heptafluoro-1-bromopentane (dried by distillation from sulfuric acid) were added. The mixture was stirred for 3 hours and refluxed for 3/4 hour. Carbon dioxide dried by passage through a calcium chloride-phosphorus pentoxide drying tube was bubbled into the Grignard solution for 30 minutes. The solution was allowed to stand overnight and then it was acidified with 3 ml. of sulfuric acid and 20 ml. of ice water. The ether layer was separated and dried over anhydrous sodium sulfate. Removal of the ether by distillation and distillation of the residue yielded a material boiling at 85-165°, the higher boiling fraction crystallizing in the condenser. Redistillation at 7 mm. pressure gave material boiling at 49-69°. The crude product was dissolved in dilute sodium carbonate, extracted with ether, and the ether solution discarded. The alkaline solution was acidified and the purified product taken up by ether extraction. Evaporation of the ether solution followed by sublimation of the residue under reduced pressure at 90-100° gave 0.12 g. of white flakey product identified as 4,4,5,5,6,6,6-heptafluorohexanoic acid, and melting at 36-37°.

Analysis. Calculated for $C_6H_5F_7O_2$: C, 29.76; H, 2.08; N. E., 242.1.
Found: C, 29.96; H, 2.24; N. E., 238.

Substituted Chlorosilanes from 3,3,4,4,5,5,5-Hpetafluoro-1-bromo pentane. In a 2-liter 3-neck flask equipped with mercury seal stirrer, dropping funnel, and condenser attached to nitrogen inlet and pressure regulator was placed 6.2 g. (0.25 mole) of magnesium ribbon. The apparatus and magnesium were dried by heating with a flame while passing nitrogen through. After placing

650 ml. of dry ether in the reaction flask, 66.7 g. (0.24 mole) of 3,3,4,4,5,5,5-
heptafluoro-1-bromopentane and 125 ml. of dry ether in the dropping funnel,
the stirrer was started. The bromide was allowed to drop into the reaction
flask fairly rapidly in order to maintain a rapid reaction. When reaction was
complete the mixture was cooled in an ice bath and 20.7 g. (0.12 mole) of sili-
con tetrachloride and 125 ml. of dry benzene placed in the dropping funnel.
With rapid stirring the contents of the dropping funnel were rapidly added to
the Grignard solution, and the mixture allowed to warm up and stand two days.
The mixture was refluxed for ten hours and most of the ether removed by distil-
lation. Dry benzene was then added in portions to the reaction mixture while
removing ether and benzene by distillation. This solvent replacement procedure
was continued until the distillate boiled at 80°, the boiling point of benzene.
The benzene solution of silanes was then decanted as well as possible from the
precipitate of inorganic salt, and the silane solution fractionated through a
Todd column with glass spiral. The distillation was carried out at atmospheric
pressure until the benzene was removed and then at 25 mm. to fractionate the
chlorosilanes. Three fractions were obtained of which the highest boiling
fraction was by far the largest: 3.88 g. boiling at 65-74°, 5.71 g. boiling
at 105-111°, and 26.38 g. boiling at 142-146°.

It is certain that the silane fraction boiling at 141-146° at 25
mm. is the tri-substituted silane and therefore the desired di-substituted
silane is probably the 105-116° fraction obtained in much smaller amount. Two
variations of the above technique, as summarized in Table III, were tried in an
effort to bring about relatively more di-substitution. These variations
failed to change the high ratio of tri and/or tetra-substitution to lower
substitution.

Table III

Substitution Method	Wt. Bromide	Wt. SiCl₄	Weights of chlorosilane fractions (25mm)			
			65-74°	105-116°	141-146°	146-165°
A	66.7 g. (0.24 mole)	20.7 g. (0.12 mole)	3.8 g.	5.7 g.	26.4 g.	
B	67.5 g. (0.24 mole)	24.8 g. (0.15 mole)	1.5 g.	3.5 g.	25.0 g.	
C	67.9 g. (0.25 mole)	42.3 g. (0.25 mole)	8.5 g.	5.5 g.	17.0 g.	
C	34.8 g. (0.13 mole)	19.5 g. (0.12 mole)	2.2 g.	3.7 g.	3.8 g.	6.0 g.

Method A: As described in full above the technique involves
adding a benzene solution of silicon tetrachloride rapidly to rapidly stirred
ether-Grignard solution, allowing the mixture to stand 48 hours, and reflux-
ing to insure complete reaction.

Method B: The Grignard solution was transferred to the dropping
funnel taking care to exclude moisture, and the Grignard solution dropped
slowly with stirring into silicon tetrachloride in ether.

Method C: Most of the ether of the Grignard solution was replaced
with benzene by distillation technique, and this ether-benzene Grignard solu-
tion was dropped slowly into refluxing silicon tetrachloride in benzene.

Table IV

Analyses

B.P. at 25 mm.	Proposed formula	C Calcd. Found		H Calcd. Found		F Calcd. Found		Cl Calcd. Found	
72-74°	$(C_3F_7CH_2CH_2)_4$ Si					65.16	62.22	0.00	1.73
"	"					"	62.75	"	1.98
141-145°	$(C_3F_7CH_2CH_2)_3$ SiCl	27.51	28.27	1.84	2.21	60.93	64.82	5.42	1.11
"	"					"	58.82	"	6.38
"	"	"	26.62	"	2.28			"	5.36

Substituted Ethoxysilanes from 3,3,4,4,5,5,5-Heptafluoro-1-bromopentane.

In a 1-liter 3-neck flask equipped with dropping funnel, mercury seal stirrer, condenser and inlet for nitrogen at the top of the condenser connected to a pressure regulator was placed 8.0 g. (0.33 mole) of magnesium ribbon. Moisture was driven from the apparatus and magnesium by heating in a stream of dry nitrogen; the condenser was heated in an over. To the flask were added 525 ml. of anhydrous ether and 31.71 g. (0.15 mole) of freshly distilled ethyl silicate, and to the dropping funnel were added 125 ml. of dry ether and 83.15 g. (0.30 mole) of 3,3,4,4,5,5,5-heptafluoro-1-bromopentane. With stirring, the bromide solution was dropped into the reaction flask over a period of four hours. Most of the ether was removed from the ethoxysilane solution by distillation, and dry benzene added in portions with continued distillation until the distillate boiled at 80°. The benzene solution of ethoxysilanes was separated from the sediment of inorganic salt by decantation and centrifugation, taking care to minimize contact with moist air. The solution was then concentrated by distillation and the residue of ethoxysilanes fractionated through a glass spiral packed Todd column at 25 mm. The fractions obtained were: 7.44 g. boiling at 71-78°, 3.0 g. boiling at 89-93°, 16 g. boiling at 93°, 2.7 g. boiling at 93-110°, and 17.3 g. boiling at 119-130°. Assuming the fraction obtained in largest amount, the 93° boiling fraction, to be the desired di-substituted ethoxysilane the per cent conversion would be 20. The simple technique just described seems most suitable for the preparation of ethoxy-silanes as the following Table V shows. The more involved method of pre-paring the Grignard solution separately and transferring to a dropping fun-nel followed by addition to the ethyl silicate solution does not give a bet-ter yield of the desired product.

Table V

Exp. No.	Wt. Bromide	Wt. Ethyl silicate	Method	Ethoxysilane Fractions at 25 mm.		
				Wt., grams	B.P. °C.	*% yield
1	43.7 g. (0.16 mole)	12.1 g. (0.058 mole)	Ac	3.06 7.99	55 (18 mm.) 73-80 (20 mm.)	
2	43.6 g. (0.16 mole)	15.0 g. (0.072 mole)	B	2.25 10.19 6.77	78-74 89-96 105-118	24
3	43.4 g. (0.16 mole)	15.8 g. (0.076 mole)	Ab	2.64 11.92 9.00	70-86 90-96 105-117	28
4	45.2 g. (0.16 mole)	15.9 g. (0.076 mole)	Ac	8.20	69-86	
5	46.2 g. (0.17 mole)	16.87 g. (0.078 mole)	Aa[x]	5.02 10.60	71-88 90-92	24.8
6	40.99 g. (0.15 mole)	13.95 g. (0.077 mole)	C[x]	6.30 11.35	70-80 86-92	29
7	83.15 g. (0.30 mole)	31.7 g. (0.15 mole)	C[y]	7.44 3.0 16.0 2.7 17.3	71-78 89-93 93 93-110 119-130	20

*Yield based on bromide assuming that the indicated fraction is di-substituted ethoxysilane.

[x]Chloroform used in place of benzene for the solvent exchange technique.

[y]Magnesium salt removed from benzene solution of ethoxysilanes by centrifugation.

The three major methods, A, B, C, of conducting this replacement reaction were modified in various ways to give methods Aa, Ab, etc. In method A the Grignard solution was dropped into a solution of ethyl silicate whereas in method B the reverse method of addition was used. In method C the so-called direct method of Grignard replacement was used, in which the bromide solution was dropped into an ether solution of ethyl silicate and magnesium ribbon.

Method Aa: The ether solution of the Grignard reagent was dropped

into the ether solution of ethyl silicate with simultaneous distillation to remove ether.

Method Ab: The ether solution of the Grignard reagent was dropped slowly into a benzene solution of ethyl silicate.

Method Ac: Most of the ether of the Grignard solution was replaced with benzene by distillation technique and the benzene-ether-Grignard solution was dropped slowly into refluxing solution of ethyl silicate in benzene.

Method B: The ethyl silicate in benzene was quickly added to the ether solution of the Grignard reagent with stirring.

Method C: The heptafluoropentyl bromide in ether was dropped slowly into a mixture of ethyl silicate, ether and magnesium ribbon thus generating the Grignard reagent in the presence of ethyl silicate. It can be presumed that the ethyl silicate reacts at once with the Grignard reagent as it forms.

Table VI

Analyses

B.P. at 25 mm.	Proposed Formula	C		H	
		Calcd.	Found	Calcd.	Found
70-75°	$(C_3F_7CH_2CH_2)-Si(OC_2H_5)_3$	36.66	34.71	5.31	3.99
90-92°	$(C_3F_7CH_2CH_2)_2-Si(OC_2H_5)_2$	32.82	33.75	3.54	5.76

Derivatives of Intermediates in Silane Preparation

1,1,1,2,2,3,3-Heptafluoropentane. A mixture of 3,3,4,4,5,5,5-heptafluoro-1-pentene (20 g., 0.1 mole), 25 ml. of methylcyclohexane, and 0.2 g. of platinum oxide was placed in a Parr low pressure hydrogenation apparatus. After reduction the catalyst was removed by filtration and the filtrate rectified, affording 9.1 g. (45.3%) of 1,1,1,2,2,3,3-heptafluoropentane boiling at 39°.

A second experiment using 50 g. (0.255 mole) of olefin led to the isolation of 40 g. (79.2%) of heptafluoropentane boiling at 39°.

Attempts at Bromination of 1,1,1,2,2,3,3-Heptafluoropentane. An attempt to brominate heptafluoropentane in the vapor phase over Columbia activated carbon at temperatures up to 250° led only to the isolation of starting material. The apparatus used was similar to that used for HBr addition to heptafluoropentene.

Treatment of heptafluoropentane with N-bromosuccinimide and benzoyl peroxide in refluxing carbon tetrachloride solution for 7 hours failed to bring about bromination.

3,3,4,4,5,5,5-Heptafluoro-1,2-dibromopentane. The vapor phase apparatus used for HBr addition was employed. In the olefin vaporizing flask were placed 53.8 g. (0.27 mole) of 3,3,4,4,5,5,5-heptafluoro-1-pentene and 33.5 g. (0.21 mole) of bromine. The reaction tube was packed with 58 g. of 20-48 mesh Columbia activated carbon, freshly activated by heating to 200° for 3 hours under vacuum. The temperature of the reaction chamber was gradually increased from 114° to 143° over a period of 4.5 hours, the period during which the olefin and bromine was being forced through the reaction tube. More bromine (10 g., 0.062 mole) was added at the end of 3 hours and 8 g. (0.05 mole) of bromine was added at the end of 4 hours. The voltage of the olefin vaporizing flask mantle was increased from 15 to 25 during the run. The crude product was shaken with aqueous sodium bisulfite to remove excess bromine, and combined with ether extracts of the water layer. The ether solution of product was dried over drierite and distilled to remove ether. The residue was fractionated through a Todd column equipped with wire spiral. There was obtained 6.3 g. boiling at 140-140.5°, 8.08 g. boiling at 140.5-141°, and 9.01 g.

boiling at 141° (a sample sent in for analysis), and 22.5 g. boiling at 141°.
The total product boiling at 140-141° weighed 45.9 g. (0.13 mole, 48%).
Analysis. Calculated for $C_5H_3F_7Br_2$: C, 16.87; H, 0.85; Br, 44.93. Found:
C, 16.87; H, 1.00; Br, 44.74.

3,3,4,4,5,5,5-Heptafluoropentyl Acetate. (1) To 27.6 g. of 2.5%
boron trifluoride in glacial acetic acid was added 25.4 g. of 3,3,4,4,5,5,5-
heptafluoro-1-pentene. The mixture was allowed to stand in a glass stoppered
flask at room temperature in a dark place for 6 days. Distillation through
a Todd column packed with metal spiral gave 19 grams of olefin startin
material. Distillation of the last portion of acetic acid solution through a
short helice packed column afforded 2 ml. boiling at 138-140° which may be
presumed to be impure heptafluoropentyl acetate. This acetate prepared by
another method (replacement reaction between heptafluoropentyl bromide and
acetate) was found to boil at 136.5°.

(2) Out of a mixture consisting of 10.9 g. (0.039 mole) of heptafluoro-
pentyl bromide, 24.6 g. (0.3 mole) of anhydrous sodium acetate, and 100 ml.
of water, an oil separated which on isolation was found to weigh 5.65 g. Distil-
lation of this oil through a short helice packed column gave 2.32 g. (0.009
mole, 23%) of liquid product having a characteristic ester odor and boiling
at 136.5°. The refractive index at 20° was 1.3271. The product gave the
characteristic odor of 3,3,4,4,5,5,5-heptafluoro-1-pentanol when treated with
hot 50% aqueous sodium hydroxide. Therefore, the product was assumed to be
the desired heptafluoropentyl acetate.

3,3,4,4,5,5,5-Heptafluoro-1-iodopentane. A mixture consisting of
10.3 g. (0.037 mole) of heptafluoropentyl bromide, 20 g. (0.13 mole) of
sodium iodide, 10 ml. of water, and 40 ml. of acetone was refluxed for 42 hours.
After removal of acetone from the reaction mixture by distillation the remaining

solution was extracted with ether and the ether solution dried over drierite. Distillation then afforded, after removal of ether, 3.8 g. of iodine saturated product boiling at 116-117°. The yield including the column holdup was 6.0 g. (0.019 mole, 51%). The product gave a precipitate with alcoholic silver nitrate on standing several hours at room temperature. This yellow precipitate was shown to be silver iodide.

Attempt to Prepare 3,3,4,4,5,5,5-Heptafluoro-1-pentanol. (1) A mixture consisting of 19 g. (0.068 mole) of 3,3,4,4,5,5,5-heptafluoro-1-bromo-pentane, 6.0 g. (0.071 mole) of sodium bicarbonate, 30 ml. of acetone and 20 ml. of water was refluxed for 8.5 hours. Six hours after the start of the heating period carbon dioxide was still being rapidly evolved from the reaction mixture as detected by connecting tubing between the top of the condenser and a tube filled with barium hydroxide solution; carbon dioxide from the reaction mixture gave a precipitate of barium carbonate. The reaction mixture was distilled to remove most of the acetone and the residue diluted with water. The bottom oily layer was drawn off and combined with three ether extractions of the water layer. After drying the ether solution over drierite it was fractionated. Only starting material and low boiling material was obtained. The desired pentanol boils at 116°.

(2) To 4 g. (0.071 mole) of potassium hydroxide dissolved in 60 ml. of 95% ethanol and 10 ml. of water and cooled in an ice bath was added 18.1 g. (0.065 mole) of heptafluoropentyl bromide. This homogeneous solution was then placed in the freezing compartment of a refrigerator and allowed to stand 44 hours. At the end of this period the bottom of the flask was found to be covered with white crystals of potassium bromide. The solution was decanted from the crystals, acidified with hydrochloric acid, and diluted with 200 ml. of water. The lower oily layer was drawn off and distilled in

a small distilling flask. Of the 6.3 g. of oil about 75% was found to boil at 32-40° and was impure 3,3,4,4,5,5,5-heptafluoro-1-pentene. The remaining 25% boiled at near 97° and was the starting material.

Hydrolyses of Chloro and Ethoxysilanes

Hydrolysis of Fluorinated Alkylchloro Silane boiling at 106-116° at 25 mm.

On shaking 12.6 g. of this silane with 20 ml. of water the mixture became warm. The mixture was refluxed for 4.5 hours and the lower brown oily layer taken up by ether extraction. After drying the ether solution with drierite it was fractionated, the final portion of oil fractionated at 2 mm. to give fractions boiling at 74-95° and 140-180° in small amounts. The residue in the still pot turned dark but did not distill at a pot temperature of 250°. These materials are being investigated.

Tris-(3,3,4,4,5,5,5-heptafluoropentyl) Silanol.

To 46.8 g. of fluorinated alkylchlorosilane (b.p. = 141-146° at 25 mm.) was added 50 ml. of water and the mixture refluxed for seven hours. The oily layer was then taken up by ether extraction, the ether solution dried over drierite, and the ether removed from the residual product by distillation. Fractionation at 25 mm. through a glass spiral packed Todd column gave 0.5 g. boiling at 137.5° (n_D^{20}=1.3314), 1.62 g. boiling at 146° (n_D^{20}=1.3324) 7.59 g. boiling at 149-151° (R.I. = 1.3352), 9.25 g. boiling at 151-153° (n_D^{20}=1.3378), a small amount boiling at 148° at 20 mm. (n_D^{20}=1.3382), and a small amount boiling at 148° at 15 mm. (n_D^{20}=1.3382). A sample of the 151-153° fraction was analyzed.
Analysis. Calculated for $C_{15}H_{13}F_{21}OSi$: C, 28.31; H, 2.05; F, 62.70.
Found: C, 28.19; H, 2.41, F, 65.34.

These results obtained on hydrolysis indicate that the alkylchlorosilane boiling at 141-146° at 25 mm. is tris-(3,3,4,4,5,5,5-heptafluoropentyl) chlorosilane.
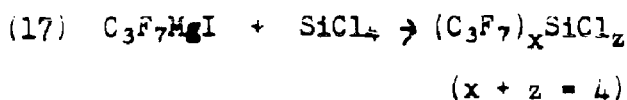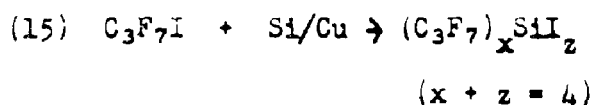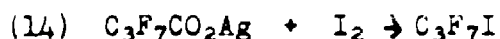
Hexaksis (3,3,4,4,5,5,5-heptafluoropentyl) disiloxane. Some tris-(3,3,4,4,5,5,5-heptafluoropentyl)silanol was refluxed with 20 ml. of acetic acid and 5 ml. of hydrochloric acid for 64 hours. The crystals which formed on the bottom of the flask were isolated by decantation to remove supernatant liquid and recrystallized from chloroform. White crystals were obtained melting at 65-66°. Recrystallization again using high boiling ligroin gave crystals melting at 66.5-67°. Final crystallization from methanol and 95% ethanol gave crystals melting at 66.5-67°. This product burns in the bunsen flame. Analysis. Calculated for $C_{30}H_{24}F_{42}OSi_2$: C, 28.72; H, 1.93. Found C, 28.01; H, 2.31.

Hydrolysis of Fluoronated Alkylethoxy Silanes boiling at 90-92° at 25 mm.

To 11.6 g. of the silane was added 20 ml. of water and 10 ml. of ammonia water. The two-layered mixture was refluxed for 10 hours. A viscous oily layer was obtained which was insoluble in ether. Further investigations are being conducted.

(c) Attempted Preparation of (Heptafluoropropyl) Silanes.

Two methods of preparation have been studied:(1) reaction of 1-iodo-heptafluoropropane with silicon-copper, and (2) preparation and reaction of heptafluoropropyl magnesium iodide with silicon tetrachloride. Experimental details are discussed in the following section. The reactions employed are illustrated as follows:

(13) $C_3F_7CO_2H$ +   AgOH → $C_3F_7CO_2Ag$

(14) $C_3F_7CO_2Ag$ + I_2 → C_3F_7I

(15) C_3F_7I +   Si/Cu → $(C_3F_7)_xSiI_z$

$(x + z = 4)$

(16) C_3F_7I +   Mg/Ether → C_3F_7MgI

(17) C_3F_7MgI + $SiCl_4$ → $(C_3F_7)_xSiCl_z$

$(x + z = 4)$

Preparation of Silver Heptafluorobutyrate. Sodium hydroxide, 240 g. (6 moles) was added to a solution of 510 g. (3 moles) of silver nitrate in 900 ml. of distilled water. The precipitate of silver oxide was filtered with suction through a sintered glass funnel and washed several times with water. Silver oxide was suspended in about two liters of distilled water and there was added 642 g. (3 moles) of heptafluorobutyric acid. The resulting solution was filtered while hot, and the filtrate was concentrated by evaporatio: . Practically 100% yield of silver heptafluorobutyrate was obtained by combining several crops which were dried on a steam cone under reduced pressure.

Preparation of heptafluoro-1-iodopropane. One mole of silver heptafluorobutyrate (321 g.) was mixed with 300 g. (1 mole) of iodine and packed loosely in a glass tube (32 mm. in diameter and 50 cm. in length), closed at one end. An ice cooled trap, followed by a dry ice cooled trap, was connected to the open end of the tube, and to the outlet from the second trap was connected a water bubbler to allow the observation of carbon dioxide emmission. Gentle heat was applied to a localized region at the closed end of the tube and as carbon dioxide emmission slowed, the flame was moved down the length of the tube. The liquid in the two traps was washed with sodium bisulfite and water, and then dried over Drierite. Distillation through a short Vigreaux column yielded the desired product, b.p. 39-40°.

Reaction of Heptafluoro-1-iodopropane with Silicon-Copper. Silicon-copper alloy, pulverized to 40 mesh, was packed loosely between plugs of glass wool in a glass tube that was connected to a water-cooled condenser, followed by a dry ice cooled condenser which, in turn, was connected to a mercury manometer. Two inlet tubes, one for the alkyl iodide and the other for nitrogen gas were placed on the opposite end of the tube. The glass tube, containing the powdered silicon-copper, was heated in a tube furnace to 300°C

and 75 g. of heptafluoro-1-iodopropane was added slowly over a five hour period (15 g./1Hr.) with oxygen-free nitrogen gas used as a diluent. There was obtained a small amount of liquid in the water cooled trap and a greater amount in the dry ice cooled trap. Upon distillation through the Todd column, containing a wire spiral, there was obtained 50 g. of material, b.p. 39-40°C., representing a 66% recovery of starting material. No other product was isolated.

The various experiments are outlined as follows:

Table VII

Run	Temperature	Rate	Percent of Recovered Material	Products
1	300°	15 hrs. (3.3 g. 1 hr)	50%	39-40°C (25 g.)
2	300	5 hrs. (15 g. 1 hr)	66%	39-40°C (50 g.)
3	350°	5 hrs. (15 g. 1 hr)	33%	39-40°C (16 g.)
				40-55°C (2 g.)
				55-56°C (7 g.)
4	400°	—At 400°, using 40 mesh, sintering of the silicon copper takes place and one must use approximately 20 mesh materials.		
5	500°	8 hrs. (9 g. 1 hr)	26%	40-49° (8 g.)
				55-56° (10.5 g.)
6	475°	8 hrs. (9 g. 1 hr)	15%	55-56° (20 g.)

The material boiling at 55-56°C was analyzed and was identified as C_6F_{14} which might form from the coupling of heptafluoropropyl radicals.

Analysis. Calcd. for C_6F_{14}: C, 21.3; H, 0.

Found: C, 21.0; H, 0.13.

Preparation and Reactions of Heptafluoropropyl Magnesium Iodide.

Preparation of 3,3,4,4,5,5,5-heptafluoro-2-methyl-2-pentanol.

Magnesium turnings, 6 g. (0.25 moles), were placed in a 3-necked, round bottomed

flask fitted with an efficient stirrer, separatory funnel, and reflux con-

denser to which was attached a dry-ice cooled trap. The entire apparatus

was dried, and 100 ml. of dry tetrahydrofuran was added. A small amount of

heptafluoro-1-iodopropane was introduced into the reaction flask at room

temperature and the mixture was stirred vigorously until reaction had started

as indicated by evolution of heat and the formation of a brown precipitate.

The reaction flask was cooled immediately to -30 to -40°C, and maintained

at this temperature during the addition of 74 g. (0.25 moles) of heptafluoro-

1-iodopropane. The extent of the reaction was followed by the formation of

a precipitate as the magnesium metal disappeared. The reaction became

exothermic in those experiments when cooling of the reaction flask was not

accomplished immediately following initiation of Gregnard formation. When

all the halide had been added, stirring was continued for two hours.

Acetone, 29 g. (0.5 moles) was added dropwise at -30°C. and the

reaction temperature was allowed to rise gradually to 25°C. The reaction

mixture was then hydrolyzed with water resulting in the formation of magne-

sium salts. The contents of the flask were then poured onto a 10% sulfuric

acid-ice mixture. Upon rectification, there was obtained 20 g. of unreacted

heptafluoro-1-iodopropane and 12 g. of 3,3,4,4,5,5,5-heptafluoro-2-methyl-2-

pentanol, b.p. 107-108°C., n_D^{20}=1.3250 which represents a conversion of 21%

and a 48% yield. Assignment of the structure was based on agreement with

the reported properties of the tertiary alcohol.

Preparation of 1,1,1-trifluoro-3,3,4,4,5,5,5-heptafluoro-2-penta-

none. The Grignard reagent was prepared as previously described. Ethyl

trifluoroacetate, 18 g. (0.12 moles), was added dropwise to the reaction

flask and the temperature of the materials was allowed to warm to 25°C. Heat

was evolved and a gummy precipitate formed. The materials were stirred at

50° for several hours. The reaction products were then heated to reflux and,

upon cooling, were hydrolyzed with a 10% sulfuric acid-ice mixture. Upon

rectification, there were obtained 18 g. (24%) of unreacted heptafluoro-1-

iodopropane and 22.1 g. of material, b.p. 104-105°C., n_D^{20} 1.3449, d_4^{20} 1.388.

Since the infrared spectrum indicated the presence of a solvated ketone,

this material was heated with phosphorus pentoxide and there was obtained

15 g. (0.06 moles) of the ketone, $CF_3\text{-}\overset{\overset{\text{O}}{\|}}{C}\text{-}C_3F_7$, b.p. 30-31°C, which represents

a yield of 50% of the theoretical.

Anal. Calcd. for $C_5F_{10}O$: C, 22.57; H, 0; F, 71.4

Found: C, 22.28; H, 0.016; F, 70.0

Attempts to prepare the 2,4-dinitrophenyl hydrozone of 1,1,1-tri-
fluoro-3,3,4,4,5,5,5-heptafluoro-2-pentanone. A solution of 0.1 g. of 2,4-
dinitrophenyl-hydrozone and 20 ml. of ethanol was treated with both the solvated

and the non-solvated ketone. The resulting solution, in each case, was heated

to boiling and, upon standing, a precipitate formed. This substance decomposed

to 150° and was not stable to recrystallization.

Preparation of 1,1,1,2,2,3,3,5,5,6,6,7,7,-tetradecafluoro-4-heptanol.
Heptafluorobutyraldehyde, 60 g. (0.3 moles) was added dropwise to the Grignard

reagent (100 g. of heptafluoro-1-iodopropane and 8 g. of magnesium turnings).

Upon reaching room temperature the precipitate became so viscous that addi-

tional solvent was added in order to continue stirring the reaction mixture.

Following hydrolysis and rectification there was obtained 40 g. of material,

b.p. 94-95°C, n_D^{20} 1.317 d_4^{20} 1.39. Both the infrared spectrum and analytical

data indicated that the alcohol was contaminated with less than one percent

of tetrahydrofuran, and it was found necessary to isolate the alcohol as the 3,5-dinitrobenzoate ester, m.p. 106-107°C. The conversion obtained in this manner represents 33% of the theoretical.

Anal. Calc. for $C_{14}H_4O_6N_2F_{14}$: C, 30; H, 0.8

Found: C, 30.3; H, 0.98

Reaction of the Grignard reagent with 1,1,1-trifluoro-2-propanone.

1,1,1-Trifluoro-2-propanone, 25 g. (0.25 moles). was added slowly to the Grignard reagent and the products were treated as previously described (the techniques of the reaction are such that it is inconvenient to add the Grignard reagent to 1,1,1-trifluoro-2-propanone). Distillation of the reaction mixture resulted in sublimation of 27 g. of a solid which, recrystallized from a mixture of benzene and petroleum ether, melted sharply at 92-94°C. There are indications that this material is a polymer of 1,1,1-trifluoro-2-propanone.

Anal. Calc. for $C_3H_3F_3O$: C, 32.1; H, 2.67

Found: C, 30.5; H, 2.63.

Attempt to prepare heptafluorobutyric acid. The Grignard reagent was prepared as previously described. At the completion of formation of the reagent, the reaction materials were poured onto slurry of 200 g. of solid carbon dioxide and ethyl ether, and were then stirred for several hours. The products were then hydrolyzed with 20% sulfuric acid-ice mixture. Upon extraction with ether and rectification, there was obtained no high boiling materials, and this indicated that the desired acid did not form.

Attempt to prepare 3,3,4,4,5,5,5-Heptafluoro-2-pentanol. Acetaldehyde, 17 g. (0.38 moles), was added to the Grignard reagent. The reaction materials were hydrolyzed, extracted with ether, dried and rectified. There were obtained only a few drops of material boiling at approximately 100°C. A large quantity of tars were isolated in this reaction, and therefore no

further attempt was made to identify the products.

Attempts to prepare the Grignard reagent in solvents other than tetrahydrofuran. 1. Anisole. The method previously described to initiate the formation of the Grignard reagent in tetrahydrofuran was unsuccessful in anisole. The reaction mixture was heated and stirred for several hours without initiating the reaction. Furthermore, both the addition of a crystal of iodine and a small amount of methyl iodide failed to initiate Grignard formation. However, the addition of a small amount of ethyl ether initiated the reaction and the flask was then cooled and maintained at 0°C. Heptafluoro-1-iodopropane, 100 g. (0.33 moles), was added dropwise during a three hour period, and the reaction products were stirred at 0°C for an additional two hours. Acetone, 20 g., was then added and the reaction flask was maintained at 50°C. for several hours. The materials were then hydrolyzed with a saturated ammonium chloride solution and there was subsequently obtained 8 g. of 3,3,4,4,5,5,5-heptafluoro-2-methyl-2-pentanol, b.p. 107-108°C., n_D^{20} 1.3250 which represents a conversion of 12% of the theoretical.

2. Butyl ether. It was found impossible to maintain the formation of the Grignard reagent in butyl ether at temperatures lower than 25°C. The addition of acetone to Grignard reagent formed at 25°C. yielded only a small quantity of the desired alcohol.

3. Ethyl ether. Heat is evolved in the reaction of heptafluoro-1-iodopropane with magnesium metal in ethyl ether. The principal products of the reaction at 25°C. are C_3F_7H and $CF_3-CF=CF_2$. Various attempts to carry out the reaction at temperatures lower than 25°C. failed as the formation of the Grignard reagent stopped at these temperatures.

Attempts to prepare a fluorine containing silane. 1. Tetraethyl orthosilicate, 35 g., was added to the Grignard reagent and the mixture was

stirred for several hours. Considerable polymeric materials appeared indicating an attack on the solvent, tetrahydrofuran. Upon rectification, there was recovered 25 g. of ethyl silicate, indicating that reaction of the Grignard reagent with the ortho ester had not occurred.

2. The techniques described above were repeated in anisole solvent and only polymeric materials were isolated.

3. Trimethylchlorosilane, 35 g., was added to the Grignard reagent in an attempt to replace the chlorine with a heptafluoropropyl group. The mixture was stirred for several hours and some five grams of material, b.p. 25-30°C., were distilled away from the polymeric materials. An infrared spectrum indicates that no fluorine is present in this low boiling compound.

4. Silicon tetrachloride, 20 g., was added to the Grignard reagent and the mixture was allowed to warm from -40°C. to 25°C. There were indications that a low boiling gas evolved and further studies are being made with this system.

Effect of Dilution of the formation of Grignard Reagent. Using 30 ml. of tetrahydrofuran in an experiment involving one-fourth of a mole of both magnesium and heptafluoro-1-iodopropane, there was obtained approximately 10% of the addition product of the Grignard with acetone. Under similar conditions, with the exception that 100 ml. of tetrahydrofuran was used, it has been pointed out previously that the yield of 3,3,4,4,5,5,5-heptafloro-2-methyl -2-pentanol was 21%. In 200 ml. of tetrahydrofuran, the Grignard formation was difficult to initiate and maintain at low temperatures although the yield of desired alcohol was increased to a small extent.

Attempts to prepare the Grignard reagent in a small amount of solvent, followed by the addition of a quantity of solvent before adding acetone to the Grignard reagent, resulted in no increase in the yield of the desired alcohol.

It was also found that the formation of the Grignard reagent could not be initiated in the presence of acetone. Various attempts to initiate the reaction, i.e. the addition of a crystal of iodine, the addition of a few drops of methyl iodide and the application of heat, failed.

A blank determination of heptafluoro-1-iodopropane under conditions of the Grignard preparation. A mixture of 62 g. of heptafluoro-1-iodopropane and 34 g. of anisole was washed with ammonium chloride, followed by a sodium bicarbonate wash, and then washed with water. There was recovered 34 g. of heptafluoro-1-iodopropane on distillation of the dry organic layer which represents a 48% recovery.

Attempt to titrate the Grignard reagent. There was removed from a typical run 12 ml. of solution which was added to water. The precipitate which formed was dissolved in an excess of standard sulfuric acid. The dark color of the solution prevented the detection of an end point on back titration with standard sodium hydroxide.

(d). Attempted Synthesis of 3,3,3-Trifluoropropene.

The reactions studied are illustrated by the following equations:

(18) $CF_3CO_2H + LiAlH_4/Ether \rightarrow CF_3CHO$

(19) $CF_3CHO + MeMgBr \rightarrow CF_3CHOHCH_3$

(20) $CF_3CHOHCH_3 + P_2O_5 \rightarrow CF_3CH=CH_2$

Preparation of trifluoroacetaldehyde. A three necked, 5 liter flask was equipped with a reflux condenser, a mercury-sealed stirrer and a dropping funnel with pressure relief. There were placed in the flask 3.5 lbs. of dry ether and 76 g. (2 moles) of lithium aluminum hydride. The mixture was cooled in an ice-water bath and 228 g. (2 moles) of trifluoroacetic acid, diluted with an half pound of ether, was added dropwise with stirring over a 2-3 hour period. After standing overnight, the excess lithium aluminum hydride was

hydrolyzed slowly with 92 g. of 95% ethyl alcohol. The reaction mixture was then poured onto a mixture of 2 kg. of ice and 300 ml. of concentrated sulfuric acid. The solution was stirred and allowed to stand until the ether cleared The water layer was extracted three times with small amounts of ether. The ether extracts were combined and the ether removed by distillation. The remaining solution was cooled and an equal volume of concentrated sulfuric acid was added. The resulting mixture was heated to 100°C. and fluoral gas was collected in a dry ice trap over a four hour period, yield 65.4 g. (0.66 mole) or 33%.

Preparation of 1,1,1-Trifluoro-2-propanol. A one liter, 3-neck flask was equipped with a gas inlet tube, a mercury sealed stirrer and a dry ice condenser. Methyl bromide gas was passed into a mixture of 16.8 g. (0.7 M) of magnesium turnings and one pound of dry ether. The reaction flask was cooled immediately after the start of the reaction, and methyl bromide was passed into the flask continuously until all the magnesium was used up. Fluoral, 65.4 g. (0.66 M), was introduced into the reaction flask, and some polymer formation was observed. After completion of the addition of fluoral, the flask was allowed to warm to room temperature with stirring. The reaction mixture was then poured onto 500 g. of ice and 20 ml. of concentrated sulfuric acid. The ether layer was separated and the aqueous layer was then extracted three times with small amounts of ether. The ether extract was dried with Drierite and the ether distilled. The remaining solution was distilled, using a Todd Column, and there was obtained 37 g. of 1,1,1-trifluoro-2-propanol, b.p. 77-78°C.

Attempts to prepare 3,3,3-trifluoro-1-propene. (1) A 250 ml., round bottomed flask was equipped with a "Y" tube containing a dropping funnel and a water condenser, to the top of which was attached a gas outlet tube. There was placed in the flask 34 g. of phosphorus pentoxide and the

alcohol was introduced dropwise. The mixture was heated for 5-6 hours and no olefin was detected in the dry ice-trichloroethylene trap. Additional phosphorus pentoxide was added and heating of the mixture was continued. Apparently, decomposition of the alcohol occurred as gases were detected which were not condensed in dry ice trap.
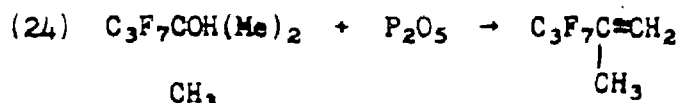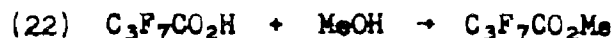
(2) The alcohol was added dropwise onto preheated phosphorus pentoxide and decomposition occurred immediately.

(3) An attempt to dehydrate the alcohol with concentrated sulfuric acid failed. Furthermore, using 30% fuming sulfuric as dehydrating agent was unsuccessful.

(4) The alcohol was dried with potassium carbonate, and redistilled. Decomposition was again detected when the dry alcohol, phosphorus pentoxide mixture was heated. No olefin was isolated.

(e). Attempted Synthesis of 3,3,4,4,5,5,5-heptafluoro-2-methyl-1-bromopentane.

In the preliminary stages of this work, the above synthesis was investigated but abandoned due to the difficulties experienced. The preparative work is illustrated as follows:

(22) $C_3F_7CO_2H$ + MeOH → $C_3F_7CO_2Me$

(23) $C_3F_7CO_2Me$ + MeMgBr → $C_3F_7COH(Me)_2$

(24) $C_3F_7COH(Me)_2$ + P_2O_5 → $C_3F_7C=CH_2$
  CH₃   CH₃

$$(24)\quad C_3F_7COH(Me)_2 + P_2O_5 \rightarrow C_3F_7\underset{\overset{|}{CH_3}}{C}=CH_2$$

(26) $C_3F_7C=CH_2$ + HBr → $C_3F_7CH(CH_3)CH_2Br$

Methyl Heptafluorobutyrate. A mixture of 856 g. (4 moles) of heptafluorobutyric acid and 155 g. (4.8 moles) of methyl alcohol was refluxed overnight. On cooling, two layers formed and the water layer was separated and discarded. An equal volume of concentrated sulfuric acid was added to the organic phase and the mixture was distilled on steam bath. There was

obtained 640 g. (2.9 moles) of the desired ester, b.p. 75-76°, a yield of 72%.

3,3,4,4,5,5,5-Heptafluoro-2-methyl-2-pentanol. Methyl bromide gas was passed into a mixture of 67 g. (2.8 moles) of magnesium turnings and a pound of ether. The reaction flask was cooled immediately after the start of the reaction, and the methyl bromide was passed into the flask continuously until all the magnesium was used up. The ester, methyl heptafluorobutyrate, in 228 g. (1 mole) amount was introduced dropwise over a period of two hours. The reaction mixture was then poured onto a mixture of 1500 g. of ice and 50 ml. of concentrated sulfuric acid. After extracting the water phase with ether there was obtained 162 g. (0.71 mole) of the desired alcohol. The yield was 71%.

3,3,4,4,5,5,5-heptafluoro-2-methyl-1-pentene. A mixture of 162 g. (0.71 mole) of 3,3,4,4,5,5,5-heptafluoro-2-methyl-2-pentanol and 350 ml. of concentrated sulfuric acid was distilled. There was obtained 135 g. (0.64 mole) of the desired pentene boiling at 55°, a yield of 90%.
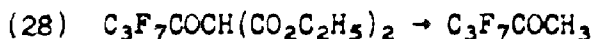
Attempted Preparation of 3,3,4,4,5,5,5-Heptafluoro-2-methyl-1-bromopentane. The apparatus used for adding HBr in the vapor phase to heptafluoropentene was employed. The reaction tube was 24 cm. long and 1.2 cm. in diameter and was filled with 12 g. of 16 mesh Columbia activated carbon, freshly reactivated by heating at 200 for three hours under reduced pressure. In the olefin vaporizing tube was placed 14.9 g. of 3,3,4,4,5,5,5-heptafluoro-2-methyl-1-pentene. Olefin and HBr were passed upward through the catalyst, along with a smaller stream of boron trifluoride, maintained at 100-112° for 2 hours, maintained at 136-165° for 1/2 hour and finally maintained at 185° for 1/2 hour. Distillation of the 10.2 g. of material left in the olefin vaporizing tube afforded only starting material boiling at 55-56°. No further experiments were conducted.

<u>3,3,4,4,5,5,5-heptafluoro-2-methylpentane.</u> In a low pressure Parr hydrogenation apparatus was placed 21 g. (0.1 mole) of 3,3,4,4,5,5,5-hepta-fluoro-2-methyl-1-pentene, 30 ml. of methylcyclohexane, and 0.2 g. of platinum oxide. After hydrogenation was complete the catalyst was removed from the reaction mixture by filtration. Distillation afforded 16.5 g. of crude product boiling at 63°. Another rectification gave 12.6 g. (59.4%) of the desired pentane boiling at 60.5-61.5°.

In another run 50 g. (0.238 mole) of heptafluoro-2-methylpentene was reduced to give 44.5 g. (88%) of the desired pentane boiling at 60.5-61.5°.

<u>(f). Attempted Synthesis of 3,3,4,4,5,5,5-Heptafluoro-2-pentanone.</u>

The synthesis of this material was studied employing the reaction of malonic ester with heptafluorobutyryl chloride. The experimental procedures are given below. The reactions used are illustrated as follows:

(26) $C_3F_7CO_2H$ + $\phi COCl$ → C_3F_7COCl

(27) C_3F_7COCl + $CH_2(CO_2C_2H_5)_2$ → $C_3F_7COCH(CO_2C_2H_5)_2$

(28) $C_3F_7COCH(CO_2C_2H_5)_2$ → $C_3F_7COCH_3$

<u>Preparation of Heptafluorobutyryl chloride.</u> A mixture of 125 g. (0.584 mole) of heptafluorobutyric acid and 25 g. (1.78 mole) of benzoyl chloride was heated in a three-necked, round bottom flask equipped with a mercury-sealed stirrer and distillation head to yield 44 g. (32%) of hepta-fluorobutyryl chloride, b.p. 36-39°.

<u>Preparation of Heptafluorobutyryl bromide.</u> (1) A mixture of 5.15 g. (0.135 mole) of red phosphorus and 50 g. (0.234 mole) of heptafluoro-butyric acid was placed in a 100 ml., 3-necked, round bottom flask equipped with a mercury-sealed stirrer, dropping funnel, condenser, and drying tube. Bromine (37.5 g., 0.234 mole) was added slowly and reacted immediately. After the addition the mixture was refluxed for several hours. Distillation

yielded 10.5 g. (16.3%) of crude heptafluorobutyryl bromide, b.p. 57°.

(2) The preparation of the acid bromide was repeated using a slight excess of bromine. Distillation of the reaction mixture yielded 16 g. (24.8%) of the crude acid bromide.

Reaction of Malonic ester with Heptafluorobutyryl Chloride. (1) A mixture of malonic ester, heptafluorobutyryl chloride, and ether was refluxed over night. Removal of the ether and distillation under reduced pressure yielded the original malonic ester which was identified by its boiling point and index of refraction.

(2) Heptafluorobutyryl chloride was reacted with a solution of the magnesium salt of malonic ester. Acidification of the reaction mixture and removal of the ether, followed by refluxing the residue with 40% sulfuric acid to cause decarboxylation failed to yield the desired ketone.

(3) A milder medium containing acetic acid, water, and sulfuric acid was tried in order to bring about decarboxylation of the coupling product of heptafluorobutyryl chloride and malonic ester. However the ketone was not obtained.

(4) An attempt was made to isolate the coupling product of the heptafluorobutyryl chloride and the magnesium salt of malonic ester, but met with no success.

(5) Since the magnesium salt of malonic ester failed to condense with heptafluorobutyryl chloride, the sodium salt of malonic ester in ether was tried. Hydrolysis of the resulting reaction mixture again failed to yield the desired ketone.

(6) Boron trifluoride was tried as a catalyst to bring about the desired reaction. However, instead of obtaining diethyl heptafluorobutyryl-malonate, the malonic ester was recovered.

Part B - Preparation of Polymers

The three monomeric styrenes, 3-(trifluoromethyl)styrene, 3,5-bis-(trifluoromethyl)styrene, and 2,5-bis(trifluoromethyl)styrene, were both homopolymerized and copolymerized with butadiene. In the latter case, the copolymerizations were done in an emusion system using the recipe developed by Marvel and Coworkers (6,7). The rates of copolymerization were also studied. Experimental details are presented in the following section.

1. Polymerization Studies with 2,5-bis-(trifluoromethyl)styrene.

(a). Homopolymerization of 2,5-bis(trifluoromethyl)styrene. Five grams of the styrene and 5.0 mg. of benzoyl peroxide were placed in a small pyrex tube, the tube sealed and heated at 70°C. for 24 hours. The polymer was a hard,cloudy resin.

(b). Determination of the molecular weight of the homopolymer of 2,5-bis-(trifluoromethyl)styrene. The polymer sample (0.1-0.3 g.) was dissolved in 50 cc. of toluene (dried with calcium chloride and distilled from sodium) and the viscosity of the solution measured at 30.0°C. by means of a 50 cc. viscosimeter (Ostwald-Cannon-Penske type). The relative viscosity thus determined was transformed into reduced viscosity and thence into intrinsic viscosity as described elsewhere (8). The molecular weight was found to be 4.01×10^5.

Table VIII

Sample No.	Wt. polymer per 100 cc. toluene, (g)	No. of Detn's	Time of flow, sec.
1	0.3002	6	224.2
2	0.5628	6	300.1
3	0.6249	6	159.8
toluene		6	324.6

Choosing sample No. 1 as an example, the following operations were

conducted:

Relative viscosity: $\eta\, r = \dfrac{\text{flow time of sol'n}}{\text{flow time of solvent}}$

$$\eta\, r = \frac{224.2}{159.8} = 1.40$$

Specific viscosity: $\eta\, S.P. = (n_r - 1)$

$$\eta\, S.P. = 1.40 - 1 = 0.40$$

Reduced viscosity: $\eta\, sp/c = \dfrac{\text{specific viscosity}}{\text{concentration}}$
                        (g./100 cc. solution)

$$\eta\, sp/c = \frac{0.40}{0.3002} = 1.33$$

Intrinsic viscosity: (η), estimated by assuming a linear dependence between the reduced viscosity and the concentration. Extrapolation of the three values of reduced viscosity to zero concentration gave an intrinsic viscosity of 1.07. The molecular weight was then calculated from the relationship:

$$(\eta) = KM^a$$
M = molecular weight
K = 1.28×10^{-4}
a = 0.70

(c). The Rate of Copolymerization of Butadiene and 2,5-Bis(trifluoromethyl)-styrene: The rate of conversion of the monomers to the copolymer in the standard emulsion copolymerization was determined by the use of small scale runs. The following recipe was used:

2,5-Bis(trifluoromethyl)styrene	1.0 gm.
Butadiene	3.0 gm.
Water	7.2 gm.
Soap	0.2 gm.
$n\text{-}C_{12}H_{25}SH$	0.014 gm.
$K_2S_2O_8$	0.012 gm.

The soap-mercaptan-water solution and the potassium persulfate solution were prepared as described elsewhere (6,7). In a 1 ox. screw cap bottle (sealed with a rubber gasket) were placed 6.2 ml. of the soap-mercaptan-water solution and 1.0 gm. of 2,5-bis(trifluoromethyl)styrene. After the

mixture was thoroughly chilled in an ice bath, 1.0 ml. of the potassium persulfate solution was added, followed by an excess of condensed butadiene. The butadiene was allowed to evaporate until 3.0 gm. remained in the bottle, which was then capped and weighed. Five runs were made; the bottles were placed in a bath at 50 ± 1°C. and rotated end-over-end (12 rpm) for the specified periods of time. The bottles were then removed, cooled in an ice bath, weighed, vented, and a small amount of hydroquinone was added to prevent further polymerization. After standing several hours to allow the bulk of the unreacted butadiene to escape, the bottles were reweighed; aliquot samples were then immediately taken, weighed, and dried at 65°C. under reduced pressure. The experimental results are given in Tables 9 and 10.

Table IX

Run	Sample	Wt. of Copolymer + Impurities (g)	Mean Value (g)
2	I	1.48	1.49
2	II	1.50	
3	I	1.88	1.87
3	II	1.86	
4	I	2.47	2.51
4	II	2.54	
5	I	2.93	2.92
5	II	2.90	
6	I	3.62	3.66
6	II	3.70	

The correction for non-volatile impurities was taken as 0.23 gm.

Table X

Run	Time (Hrs)	Wt. of Copolymer + Impurities (g)	Wt. of Copolymer (g)	% Conversion
2	8.0	1.49	1.26	31.5
3	12.2	1.87	1.64	41.0
4	16.2	2.51	2.28	57.0
5	20.2	2.92	2.69	67.5
6	24.0	3.66	3.43	85.8

Note: Total weight of monomers: 4.0 gm.

The above data indicate a polymerization period of about 22 hours to achieve approximately 75% conversion of the monomers.

(d). Copolymerization of Butadiene and 2,5-Bis(trifluoromethyl)-styrene. A quantity of butadiene-2,5-bis(trifluoromethyl)styrene copolymer was prepared by the usual standard emulsion procedure. The following recipe was used:

2,5-Bis(trifluoromethyl)styrene	5.0 gm.
Butadiene	15.0 gm.
Water	36.0 gm.
Soap	1.0 gm.
n-$C_{12}H_{25}SH$	0.070 gm.
$K_2S_2O_8$	0.060 gm.

Four runs were made, with a polymerization period of 23.0 hours at $50 \pm 1°C$. Aliquot samples were removed prior to coagulation for the determination of the percent conversion. The runs were combined and coagulated by the addition of 100 ml. of 5% sulfuric acid. The copolymer sample was washed with three 100 ml. portions of water and the aliquot samples were dried at 65°C. under reduced pressure.

Table AI

Run	Wt. of Copolymer + Impurities (g)	Net Wt. of Copolymer (g)	% Conversion
2	17.95	16.80	84.0
3	17.02	15.87	79.4
4	18.00	16.85	84.2
5	17.58	16.43	82.2

Note: Total weight of monomers: 20.0 gm.

Although there is a relatively large variance in the percent conversion for the various runs, the data are in closer agreement with that of the rate of copolymerization runs than in the case of the butadiene-3-(trifluoromethyl)styrene copolymerization.

The copolymer sample was purified by continuous extraction with methanol in a Soxhlet extractor followed by drying at 65°C. under reduced

pressure. Total weight of recovered copolymer: 62.7 gm. A sample of this polymer was analyzed and found to contain 7.03% fluorine. This material was sent to the Materials Laboratory.

2. Polymerization Studies with 3-5-bis(trifluoromethyl)styrene.

Homopolymerization of 3,5-bis-(trifluoromethyl)styrene. Benzoyl peroxide ("Lucidol") (18.5 mg.) was placed in a glass tube as well as 1.86 g. 3,5-bis-(trifluoromethyl)styrene. Solution took place with difficulty. The tube was cooled in dry ice-acetone, sealed, and heated at $70 \pm 1°$ for 24 hours. A faintly opalescent resin was obtained. The molecular weight of the polymer was not determined due to its low solubility in toluene.

The Rate of Copolymerization of Butadiene and 3,5-bis(trifluoromethyl)styrene. The rate of conversion of the monomers to the copolymer by the standard emulsion copolymerization was determined. A soap-mercaptan-water (S-M-W) solution was prepared by dissolving 3.23 g. of soap (commercial Ivory Flakes) in water and diluting to 100 ml.; this soap solution was then added to 0.229 g. (required weight: 0.226 g.; 1% excess) of n-dodecyl mercaptan (commercial grade, not purified). A potassium persulfate solution was also prepared by dissolving 0.60 g. of potassium persulfate (Analytical Reagent grade) in 50 ml. of water.

A mixture of 6.2 ml. of the soap, mercaptan-water-solution, and 1.0 g. of 3,5-bis(trifluoromethyl)styrene (b.p. 55-57°/14 mm; n_D^{20} 1.4240) was placed in a 1 oz. screw cap bottle, sealed with a rubber gasket. After the mixture was thoroughly chilled in an ice bath, 1.0 ml. of the potassium persulfate solution was added, followed by an excess of condensed butadiene. The butadiene was allowed to evaporate until its weight was 3.0 g.; the bottle was then capped and weighed. Six runs were made; the various bottles were placed in a bath at $50 \pm 1°C$. and rotated end-over-end (33 rpm) for the

bath, weighed, vented, and reweighed. A small amount of hydroquinone was added to each latex sample. There was no indicated loss of weight during the polymerization.

Aliquot samples were removed and dried at 65° under reduced pressure.

A correction for non-volitile impurities was determined by evaporating to dryness a weight of soap, water, n-dodecyl mercaptan, and potassium persulfate equal to that used in the copolymerization run. The weight of residue, 0.24 g., was the correction applied for non-volatile impurities in the calculation of percentage of conversion.

The results of the conversion study are given in Table XII.

Table XII

Run	Time (hrs)	Polymer + Impurities (g)	Impurities (g)	Polymer (g)	Monomers (g)	% Conversion
1	4.6	1.13	0.24	0.89	4.00	22.2
2	8.4	1.94	0.24	1.70	4.00	42.5
3	12.0	2.79	0.24	2.55	4.00	63.8
4	16.0	3.37	0.24	3.13	4.00	78.2
5	20.0	3.68	0.24	3.44	4.00	86.0
6	23.5	3.78	0.24	3.54	4.00	88.6

The above data indicate a period of 16 hours is required to carry out the polymerization to a 75-80% conversion of the monomers.

Copolymerization of Butadiene and 3,5-Bis(trifluoromethyl)styrene.
Two samples of the butadiene and 3,5-bis(trifluoromethyl)styrene copolymer were prepared by the standard emulsion procedure. The following recipe was used:

3,5-Bis(trifluoromethyl)styrene	5.0 g.
Butadiene	15.0 g.
Water	36.0 g.
Soap	1.0 g.
n-$C_{12}H_{25}SH$	0.070 g.
$K_2S_2O_8$	0.060 g.

The soap, n-dodecyl mercaptan, and water solution and the potassium persulfate solution were prepared as described for the rate of copolymerization of butadiene and 3,5-bis(trifluoromethyl)styrene. A mixture of 31.0 ml. of the soap-mercaptan-water solution and 5.0 g. of 3,5-bis-(trifluoromethyl)-styrene was placed in a 4 oz. screw cap bottle (sealed with a rubber gasket). After the mixture was thoroughly chilled in an ice bath, 5.0 ml. of the potassium persulfate solution was added, followed by an excess of condensed butadiene. The butadiene was allowed to evaporate until its weight was 15.0 g.; the bottle was then capped, weighed, placed in a bath at 50 ± 1° and rotated end-over-end (33 rpm) for 16 hours. The bottle was then removed, cooled, weighed, vented, and reweighed. There was no indicated loss of material during the polymerization period. Aliquot samples were removed for the determination of the percent conversion of the monomers.

Run	Air Dried Polymer (gm)	% Conversion
1	18.9	78.0
2	11.2	79.0

The percent conversion agrees with the data from the determination of the rate of conversion.

Run #1 was coagulated by pouring with stirring into 100 ml. of 5% sulfuric acid. The copolymer was washed with three 100 ml. portions of water and air dried. The filtrate and washings remained clear. Run #2 was coagulated in 100 ml. of methanol, washed with three 100 ml. portions of water, and air dried. The filtrate and washings were milky white and opaque, indicating the presence of suspended copolymer and incomplete coagulation.

The polymer was analyzed and found to contain 13.15% fluorine. This material was sent to the Materials Laboratory.

3. Polymerization Studies with 3-(Trifluoromethyl)styrene.

(a). <u>Homopolymerization of 3-(Trifluoromethyl)styrene.</u> Ten (10.0) milligrams of benzoyl peroxide ("Lucidol") were weighed into a glass tube and 2.00 g. of purified styrene added: solution occurred with some difficulty. The mixture was cooled in dry ice-acetone, the tube sealed and heated in a bath at 70 ± 1° for 24.3 hours. A hard resin was obtained, somewhat cloudy in appearance.

(b). <u>Viscosity of poly-3-(Trifluoromethyl)styrene in Toluene at 30°.</u> These viscosity measurements are essentially like those described previously and the measurements were made at 30.0°; two solutions containing varying amounts of polymer were examined.

Weight of polymer g./100 ml. solvent	Time of flow sec.	η_{sp}	η_{sp}/c
0	187.8 ± 0.4		
0.388	222.7 ± 0.1	0.19	0.48
0.689	258.6 ± 0.5	0.38	0.54

The intrinsic viscosity was estimated by assuming a linear dependence between the reduced viscosity and the concentration. Extrapolation of the two values of (ηsp/c) then gave η = 0.43. Using the relation

$$\eta = KM^a = 1.28 \times 10^{-4} \, M^{0.70}$$

proposed by Goldberg, Hohenstein and Mark (9) for polystyrene at 30°, a value of M- 1.1 x 10⁵ is obtained for this polymer. This value is considerably different from that obtained for polystyrene, and evidences some chemical difference between the two monomers.

(c). <u>Solubility Studies on poly-3-Trifluoromethylstyrene.</u> a) A polymer sample (1.0 g.) was dissolved in 2-butanone to give 100 ml. of solution. No visible turbidity could be obtained by dilution with ten times the volume of methanol. b) A polymer sample (1.35 g.) was dissolved in chloroform to give 100 ml. of solution. Ten (10.0) ml. aliquots were titrated with

methanol, to the first sign of turbidity. The following amounts of methanol were required:

> Trial #1 6.3 ml.
> #2 6.4 ml.
> #3 6.1 ml.

It appears that the amount of methanol required to precipitate the polymer from dilute chloroform solution can be reproduced. This method may therefore be used to compare the solubility behavior of polymers in a quantitative way if conducted under comparable conditions.

Precipitation of the polymer was completed by adding an excess of methanol (155 ml.) to the remainder of the solution (80 ml.). The polymer was recovered as a whitish solid, which could be filtered, air-dried, and handled with ease.

(d). <u>Rate of Copolymerization of 3-(Trifluoromethyl)styrene and Butadiene.</u> A series of small glass sample-tubes were charged in the following way: 6.2 ml. of soap-mercaptan-water solution; 1.00 ml. potassium persulfate solution; 1.0 g. styrene; excess butadiene, allowed to evaporate until 3.0 g. was left. At this time, the tube was stoppered, cooled in dry-ice-acetone, sealed, and rotated end over end in a bath at $50 \pm 1°$ for a specified interval. Then the tube was withdrawn from the bath, thoroughly chilled in ice, poured into a beaker containing 50 mg. hydroquinone, and allowed to stand about fifteen minutes. The solution was weighed, aliquot portions poured into weighed three-inch test tubes, and evaporated to dryness <u>in vacuo</u> at 64°. The weight of residue in each aliquot was determined and the total weight of residue calculated; the amount of non-polymer solids was assumed to be 0.33 g. and the amount of polymer was calculated by difference.

Sample No.	No. of hours	Wt. of residue, g.		Net Weight, g.	% Conversion
1	3	(a) 0.45	(b) 0.45	0.12	3
2	12.3	(a) 1.35		1.02	25
3	17.2	(a) 1.57	(b) 1.80	1.36	34

(e). Copolymerization of 3-(Trifluoromethyl)styrene and Butadiene on a 2-oz. scale. These reactions were conducted in the same way as those described previously. Two runs were made simultaneously for a period of two hours at 50°C.

At the end of this time, the extent of conversion into polymer was measured in the following way. An aliquot portion of the polymerization product was weighed into a 3-inch test tube containing two milligrams of hydroquinone to prevent further polymerization. The aliquot sample was then evaporated in vacuo at 64° to constant weight: six hours in an Abderhalden pistol containing acetone sufficed for this purpose. Under these conditions, it is assumed that the unreacted monomers were removed, and that the residue consisted of polymer, and the solid components of the initial charge. In blank experiments it was determined that the solid components exclusive of polymer amount to 1.62 ± 0.03 g. per 2-oz. run.

The data for Run #1 were as follows: total weight of latex 54.4 g.; weight of aliquot I 0.403 g., weight of aliquot residue 0.131, calculated weight of total residue 17.6 g.; weight of aliquot II 0.541 g.; weight of residue 0.1754 g.; calculated total weight 17.6 g. The average weight of total residue was 17.6 g., and the weight of polymer was obtained by subtracting the weight of other solids, i.e. 17.6 - 1.6 = 16.0. Since the total initial weight of monomers was 20.0 g., this corresponds to 80% conversion.

The data for Run #2, given in less detail, were as follows: calculated weight of total residue 17.3 ± 0.2 (average of two aliquot samples); weight of polymer 15.7; conversion 79%.

Run #1 was coagulated by pouring, with stirring, into 100 ml. 5% sulfuric acid. The copolymer was collected by suction filtration and washed

with 30 ml. of water. It was compact and elastic, somewhat sticky and pasty.

Run #2 was coagulated by pouring into 100 ml. methanol, collected by suction filtration, washed with 300 ml. water. The filtrate was milky and apparently contained considerable amount of polymer in fine suspension; the coagulum was therefore smaller in quantity, but less sticky and pasty. A small air-dried portion of this coagulum (2.3 g.) was exhaustively extracted with methanol in a Soxlet extractor and lost about 10% of its weight.

This material was analyzed and found to contain 11.88% fluorine. A sample of the polymer was sent to the Materials Laboratory.

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Appendix I

Literature Review of Fluorinated Styrenes and Butadienes

The isomeric styrenes with one fluorine atom on the benzene ring are known.[5,7,13,20,22,25] o-Fluorostyrene has been polymerized with ultraviolet light,[13] and p-fluorostyrene with 0.5% benzoyl peroxide at 70°.[5] The polymers are hard, brittle, clear resins.[5] All the fluorostyrenes could be copolymerized with butadiene in emulsion, the fluorinated styrenes entering the copolymer somethat more easily than styrene itself. The products were completely soluble in benzenes; for potential use in tire-tread recipes, o-fluorostyrene was rated worse than, m- better, and p- about the same as styrene.[14,15] 1,5-Difluoro-, 3,4-difluoro-, and 1-fluoro-5-chloro-styrenes have been reported in the patent literature, which states that their polymers and copolymers have advantageous electrical properties.[8]

m-Trifluoromethylstyrene is readily made from benzotrifluoride and has been prepared by a number of workers.[5,16,20,22,23] It has been polymerized by heat,[23] ultraviolet light,[16] or benzoyl peroxide,[5] in bulk[3,16,5] and in emulsion.[5] The polymer is a hard resin, resistant to heat and soluble in benzene. m-Trifluoromethylstyrene enters readily into a copolymer with butadiene, and the product was found superior to styrene in tire-tread preparations of the GR-S type;[14] superior tensile strength and plasticity were also claimed for it in the patent literature.[24] 2-Bromo-4-trifluoromethylstyrene and 4-fluoro-3-trifluoromethylstyrene have also been prepared and polymerized in bulk with 0.5% benzoyl peroxide at 70°C. give a resin. Copolymerization with butadiene was effected, but the products were not evaluated.[5]

a-Methylstyrenes have been prepared with the following substituents: 2-fluoro; 3-trifluoromethyl; and 3-trifluoromethyl-4-fluoro. These monomers did not polymerize with 0.5% benzoyl peroxide at 70° in a period of several

weeks, but they readily copolymerized with butadiene.[5] a-Trifluoromethyl-
styrene and a-difluoromethylstyrene are mentioned in the patent literature,
and the existence of their polymers and copolymers is indicated.[9]

B-Methyl-3-trifluoromethyl styrene has been made, but failed to
polymerize in bulk with 0.5% benzoyl peroxide at 70°, and to copolymerize
with butadiene in emulsion.[5]

As far as butadienes are concerned, only perfluorobutadiene[19] and
2-fluoro-3-chlorobutadiene[6] have been described. The thermal polymerization
of perfluorobutadiene has been investigated in the vapor phase, a condition
not calculated to give high molecular weight products, and the chief product
was a dimer, with perfluorocyclobutane; trimer and higher polymers also being
formed. The trimer apparently could be polymerized further on heating to 300°;
no products were even qualitatively characterized.[19] 2-Fluoro-3-chlorobutadiene
is mentioned in the patent literature, and it is claimed that its polymers
and copolymers are rubbery, vulcanizable, and resistant to solvents and oils.[6]

Clearly, their information on fluorine-containing compounds is not
sufficient to allow generalizations and predictions to be made, and it is
therefore helpful to consider briefly some of the more extensive investiga-
tions done on substituted styrenes containing other halogens. Marvel and
coworkers [14,15] prepared the emulsion copolymers of butadiene with a large number
of such monomers, and evaluated the products for their performance in tire-
tread recipes as compared to GR-S: the isomeric monochloro and monobromo-
styrenes gave rubbers of about equal quality, the 2- and 3-chlorostyrenes
giving a product possibly slightly superior; the 2,3-, 2,4-, 2,6-, and 3,5-
dichlorostyrenes gave products of equal quality, and the 2,5- and 3,4-dichloro-
styrenes made a distinctly superior rubber; the mixed tri- and tetrachloro-
styrenes gave an inferior rubber; and   pentachlorostyrene was not evaluated.

In all cases, except the pentachlorostyrene, the substituted styrene entered the copolymer easily, the monochloro compounds being more reactive than styrene, and the reactivity decreasing slowly with increasing halogen content. In no case was the solubility in benzenes significantly reduced.

A more quantitative measure of the reactivity of some monohalogenated styrenes is afforded by the copolymerization studies carried out in the Laboratories of the United States Rubber Company,[10,11,12,17,18,26,27] where the "r", and "r_2" values were determined for numerous monomer pairs. These quantities can be defined briefly as follows: in the copolymerization of styrene S and a monomer M any growing polymer chain must have either S or an M end group, RS· or RM·; RS· can add one more styrene molecule to give RSS· at a rate k_{ss}, and an M molecule to give RSM· at a rate k_{sm}; r_1 then equals k_{ss}/k_{sm}, and r_2 k_{mm}/k_{ms}. The pertinent data abstracted from various papers are tabulated below; in each case r_1 refers to the ratio k_{ss}/k_{sm}, when M is the monomer listed.

Table I

Monomer M	r_1	r_2
o-chlorostyrene[26]	1	
m-chlorostyrene[27]	0.64	1.09
m-bromostyrene[27]	0.55	1.05
p-chlorostyrene[27]	0.74	1.025
p-bromostyrene[27]	0.695	0.99
p-iodostyrene[27]	0.62	1.25
butadiene[18]	0.78	1.39
1,2-dichloropropene[2]	5.0	0.06
vinyl chloride[10]	17	0.02

Table I (Con'd)

Monomer M	r_1	r_2
vinylidine chloride[10,17]	1.85	0.085
trans-dichloroethylene[11]	37	0
cis-dichloroethylene[11]	210	0
tri-chloroethylene[10]	16	0
tetrachloroethylene[10]	185	0
hexachloropropylene[1]	very large	0

It appears from the Table that halogen substitution does not affect the relative reactivity ratios very greatly, and that fluorine substitution, for instance, could be effected if desired without radically altering the behavior of the monomer in copolymerization.

Regarding the probable ability of styrenes to add to halogenated butadienes, it is noteworthy that hexachlorobutadiene does not copolymerize with styrene. Indeed, the styryl-type radical much prefers adding a molecule of styrene than any ethylene-monomer bearing a halogen next to the double bond. Two halogens in the 1,1 position are much better for adding styryl radicals than two halogens in the 1,2 position. The **trans** configuration is more favorable than the **cis**. Most halogenated ethylene radicals show no tendency to add their own monomer.

By analogy, the possibility of polymerizing or copolymerizing highly halogenated butadienes seems remote. However, tetrafluoroethylene and chlorotrifluoroethylene have been polymerized. Also, it must be remembered that these reactivities are for radical-type reactions. Entirely different behavior has been demonstrated in styrene and its derivatives on ionic polymerization.

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